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# Chemistry of Wetlands and their Effect on Receiving Waters in Kejimkujik National Park, Nova Scotia

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# PREFACE

This report summarizes the results of three successive years of field work on wetland chemistry in Kejimkujik National Park, from 1986 to 1988. The work was carried out under the Federal Long Range Transport of Airborne Pollutants (LRTAP) program by personnel in Environment Canada, with the overall objective of evaluating the effect of wetlands on drainage water chemistry. The field work and analysis for the first year of the study, described in Chapter 4, was carried out by G.M. Wickware (G.M. Wickware and Associates, Inc.), I. Kessel-Taylor and C.D.A. Rubec (Environment Canada). The second and third years of the study, described in Chapters 5 and 6, were carried out by J.A. Wood (Environment Canada). The sampling program for the second year (1987) of the study was developed by I. Kessel-Taylor. All water quality analyses were carried out at the laboratories of the Water Quality Branch, Environment Canada, in Moncton. Peat soil samples were analyzed at the Environmental Chemistry laboratories, Victoria General Hospital, Halifax.

The results presented here focus primarily on classification of the wetlands within the Park and evaluation of the principal factors influencing wetland soil chemistry and their effect on the chemistry of receiving waters. The report also provides recommendations for future research on wetlands.

# ACKNOWLEDGMENTS

The assistance of the following Environment Canada staff is gratefully acknowledged. J. Wetzell and C. Drysdale (Canadian Parks Service) provided logistic support for sampling within the Park and D. McLeod (Applied Statistics Division, Environment Canada) carried out statistical analysis of the data.

## SUMMARY

The effect of wetlands on drainage water chemistry remains an outstanding issue of the Federal Long Range Transport of Airborne Pollutants (LRTAP) program. A distinctive feature of wetlands is the production of large amounts of organic acids. This confounds modelling of acid precipitation effects in drainage basins containing significant wetland areas. Existing acidification models are unable to predict whether changes in acidity of the watershed are due to changes in the input of mineral acids, primarily of anthropogenic origin or from changes in organic acid inputs originating from wetland soils. The problem is further compounded by a general lack of understanding about the role of wetlands in the hydrologic cycle of the drainage basin. Some investigators view wetlands as major contributors to drainage basin chemistry and hydrology. Other investigators view wetlands as relatively isolated components of the drainage basin during much of the year. Although the production of these acids is high, the actual inputs to the drainage waters might be limited owing to hydrologic factors.

There are further complications. Organic acid levels in drainage waters are not constant, instead showing a strong seasonal aspect. It is not established whether this relates to processes occurring in wetland soils. In addition, different classes of wetlands are believed to produce organic acids at different rates. Thus, wetlands cannot be grouped together as a whole in any modelling efforts of organic acid production. Instead their effects must be assessed with respect to their class.

In addition to concerns related to organic acid inputs, it is not well understood how wetlands influence major ion and metal chemistry of drainage waters. Several studies have suggested that they do have a strong influence, while other authors believe that during most of the year wetlands remain as relatively isolated components of the drainage system and have little effect on major ion chemistry and metals. There is also a paucity of information on the effects of seasonal changes in wetland soil chemistry and also wetland class on drainage chemistry.

In an attempt to answer how wetlands influence drainage water chemistry, a three-year field program was carried out in Kejimkujik National Park, Nova Scotia. The program focussed on sampling wetland soil chemistry, to determine if there is a relationship to drainage water chemistry. The emphasis was on organic acid production and also major ions and metals.

As a preliminary part of the program, a survey of most of the wetlands within the Park was carried out in order to characterize their vegetation and also to assess which classes of wetland were dominant and most likely to influence water chemistry, thereby meriting further study. Wetlands within the park were found to be dominantly bogs and nutrient-poor fens, with a paucity of other classes. These were quite distinct in their soil chemistry. Major ions and metals in the bogs were about half the level found in the fens. However, bogs and fens did not appear to exert any significantly different effects on the major ion and metal chemistry of drainage waters.

Bogs and fens did show some significant effects with regard to organic acid production and inputs to drainage chemistry. Organic carbon accumulation in surface peats of the bogs was about twice the level in the fens, implying rates of carbon oxidation and volatilization of about half the rate occurring in the fens. Higher rates of carbon oxidation appear to be associated with lower dissolved organic carbon inputs to the drainage network. Drainage waters at the bog sites had significantly higher dissolved organic carbon levels, and pH levels significantly lower, than at the fen sites. Studies of a more controlled nature would be required to establish a numerical relationship.

The seasonal aspect to the chemistry was also investigated. Drainage waters sampled showed strong and significant seasonal changes to their chemistry. The soil chemistry of the bogs and fens also showed significant seasonal changes in their chemistry in some of the major ions, carbon accumulation and pH. The changes were generally less consistent and smaller in magnitude than the changes in water chemistry. This suggests a possible relationship between the two media with regard to the seasonal aspect. However, more detailed investigations would be required to conclusively establish this.

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# 1.0 INTRODUCTION

The effect of wetlands on receiving waters remains an outstanding issue in the Federal Long Range Transport of Airborne Pollutants (LRTAP) Program. Acidification models for Canadian watersheds have been developed to address questions such as the effects of sulphur and nitrogen deposition on the chemistry of receiving waters. Clear-water acidification models, however, have failed when applied to coloured waters because they are unable to assess the relative contribution of mineral (anthropogenic) versus organic (natural) acids to the drainage water chemistry (Wright, 1983; Rogalla *et al.*, 1986).

A few studies have suggested that wetlands can exert a profound influence on the chemistry of drainage waters (Gorham *et al.*, 1987; Urban and Bayley, 1986; Urban *et al.*, 1989). Most of these studies are experimental in nature involving mass balance determinations of chemical inputs and outputs. However, other investigators (Roulette, personal communication) have suggested the opposite conclusion - that during much of the year wetlands appear to be hydrologically disconnected from the drainage network and therefore contribute relatively little to drainage chemistry. A generalized answer to this question is by no means obvious, particularly given the variability of wetlands and their complex relationship within the drainage setting.

To address the question of wetland effects a large data set of wetland properties, including both descriptive and chemical parameters, as well as drainage basin water chemistry has been assembled for the entire Atlantic region, with the objective of developing regional models of wetland effects on water chemistry in the area. Before proceeding with the task of analyzing a very large data base, a knowledge of which wetland soil parameters are most likely to influence drainage water chemistry is necessary. It remains to be shown from site specific data whether wetlands soil samples can be directly related to the drainage chemistry. Studies of this nature are rare with mineral soils and have not yet been attempted with wetland soils.

To determine how wetlands influence drainage chemistry a three-year field study program was initiated in Kejimkujik National Park calibrated watershed in 1986. Kejimkujik National Park was chosen because of the detailed background information available on this area. Waters are also brown coloured and rich in dissolved organic carbon which is believed to originate from the numerous wetlands in the area (Howell and Brooksbank, 1987). The overall goal of the program was to determine whether direct linkages can be established between the chemistry of drainage waters and wetlands soil (peat) chemistry from specific sites, and if so, whether these linkages can be modelled statistically. If such relationships occur, then they will be further used in the development of regional models of wetland influences on drainage water chemistry.

The program was carried out to address a number of specific objectives described below:

(1) Identify major wetland areas within each of the three calibrated drainage basins in the Park (Kejimkujik, Beaverskin, and Pebbleloggitch);

(2) Determine the extent and area of organic terrain (peatland) in each of the basins;

(3) Classify the wetlands and provide a general description for each including their vegetation characteristics;

(4) Establish whether there is a seasonal aspect to wetland soil chemistry in the area, and if there is, characterize the chemical changes;

(5) Determine if there are relationships which can be established between the seasonal changes in drainage water chemistry and seasonal changes in wetland soil chemistry;

(6) Determine if the dominant classes of wetlands found within the Park (e.g. bogs and fens) can be distinguished chemically. In principle, the bogs should be more oligotrophic and the fens more minerotrophic in their chemical make-up;

(7) Determine if proximity to the different classes exerts a local effect on drainage water chemistry.

The program was divided into three distinct phases. Each phase addressed a different set of the objectives described above. The successive phases of the program were carried out between 1986 and 1988, and the results of the different phases are described in Chapters 4, 5 and 6. Chapter 4 addresses objectives 1, 2 and 3; Chapter 5, objectives 4 and 6; and Chapter 6, objectives 5 and 7.

# 2.0 WETLANDS: DEFINITION AND CLASSIFICATION

A wetland is defined as an area saturated with water long enough to result in the growth of hydrophilic vegetation, poorly drained soils and biological activity adapted to a wet environment (National Wetlands Working Group, 1987). Wetlands are divided into two categories: (1) mineral wetlands, which produce little or no peat, and (2) peatlands, which are defined as wetlands having more than 40 cm of peat accumulation. The Canadian Wetland Classification System (National Wetlands Working Group, 1987) defines five classes of wetland: bog, fen, marsh, swamp and shallow open water. Only two of these classes, bogs and fens, are generally categorized as peatlands, although swamps in some regions display peaty soils. This report deals largely with the chemistry of the peatlands (bogs and fens) in the study area. A small number of swamps were also surveyed.

A *bog* is a peatland in which the water table is at or near the surface. It is generally acidic and low in nutrients and is unaffected by nutrient-rich groundwaters from surrounding soils. The surface of the bog may be raised or level and is covered chiefly with sphagnum moss and ericaceous shrubs. The peat is weakly to moderately decomposed sphagnum and woody peat underlain by sedge peat.

A *fen* receives its nutrients from groundwater sources, in addition to rainwater, and is therefore more nutrient-rich and minerotrophic. A fen is generally less acidic than a bog and its vegetation consists chiefly of sedges, grasses, reeds and brown moss along with some shrubs. A fen contains well-decomposed sedge and/or brown moss peat and the water table is normally at or near the surface.

A *swamp* is a mineral wetland with standing water or water gently flowing through pools or channels. The water table is at or near the surface and the waters are rich in nutrients. If peat is present, it is usually well-decomposed and underlain by sedge peat. Swamp vegetation is characterized by a dense cover of deciduous or coniferous trees or shrubs, herbs and some mosses.

A *marsh* is a mineral wetland or peatland that is periodically inundated by standing water which is rich in nutrients. The soil usually consists of mineral matter and occasionally, well decomposed peat. A marsh characteristically contains pools or channels interspersed with decaying sedges, grasses, rushes and reeds bordering meadows and bands of shrubs and trees.

*Shallow water* areas are defined as wetlands where the water is less than 2 m deep along lake, river, stream and coastal shores.

The wetlands described in this report are classified according to the primary and tertiary levels of the Canadian Wetland Classification System published by the National Wetlands Working Group (1987). In the case of the fens examined, they are further subdivided into two types: graminoid fens (dominated by grass-like plants) and shrub fens (dominated by shrub species).

# 3.0 DESCRIPTION OF THE STUDY AREA

## 3.1 DRAINAGE

The study area is located in southwestern Nova Scotia (Figure 3.1) and is located within Kejimkujik National Park. Sampling was carried out on three basins within the Park, including Kejimkujik, Pebbleloggitch and Beaverskin lake basins (Figure 3.2). Kejimkujik is the largest of the three basins with a total drainage area of 723 $km^2$. Kejimkujik is divided into various sub-basins shown in Figure 3.2. Beaverskin and Pebbleloggitch are relatively small basins with drainage areas of 1.0 and 1.6 $km^2$, respectively. Hydrology and morphometry of the major lakes in the study area are described in detail by Kerekes *et al.* (1986). All of the lakes in the Park are relatively shallow and oligotrophic.

Both Kejimkujik and Pebbleloggitch Lakes receive drainage from large wetland areas and consequently contain highly coloured organic waters, with colours exceeding 50 Hazen units (Kerekes and Friedman, 1985). Beaverskin Lake is regarded as a clear-water lake with a colour of less than 10 Hazen units.

## 3.2 CLIMATE

The mean annual daily temperature of the Kejimkujik area is 6.5°C, with a July mean daily temperature of 18.8°C and a January mean daily temperature of -5.0°C. The mean total annual precipitation is 1146 mm - the majority of which occurs as rainfall. Precipitation varies from year to year, ranging from a recorded minimum of 1129 mm to a maximum of 1816 mm (Gates, 1982).

A Canadian Atmospheric and Precipitation Monitoring Network (CAPMON) precipitation sampling station has been operated in Kejimkujik since 1983, measuring the pH of precipitation, as well as its chemical properties. The mean annual weighted pH of the precipitation for 1987 was 4.48, with the lowest 4-month average in May-August and the highest in September-December. More than 18% of the precipitation events were seriously acidic (pH < 4), with the most acidic event having a pH of 3.38.

## 3.3 GEOLOGY

Bedrock geology in the study area is shown in Figure 3.3. The Kejimkujik basin contains Devonian granite, Halifax slate (with quartzite) and Goldenville greywacke sandstone (Gimbarzevsky, 1975). Halifax slate occurs in Beaverskin Lake and also Pebbleloggitch Lake basins. Devonian granite is also found on the western half of Pebbleloggitch Lake basin. There is some evidence that the Halifax slate may be pyrite bearing in certain locations in this area, as occurs with this formation in other parts of the Province. However, there is no evidence that this affects the chemistry of any of the streams surveyed in this study.

The area was heavily glaciated during the Wisconsin and a mantle of stony coarse-textured till covers the area. The till, derived primarily from granitic, gneissic, and quartzitic bedrock material, is acidic and releases few nutrients. Typical composition of the till derived from Devonian granite is 20-35% quartz, 40-55% feldspars, and 15-20% micas (Eastern Ecological Research Ltd., 1976). Numerous drumlins and other morainal landforms are found throughout the study area (Figure 3.4). Some of the till has been reworked in glaciofluvial deposits as outwash plain, kames, eskers and deltas in the southwestern part of the Park. Post-glacial alluvial and peat deposits occur along the floodplains of modern streams and in depressions occupying former lakes.

## 3.4 SOILS

Soils of the area are predominately Orthic Humo-Ferric Podzols developed on coarse textured tills. Gleyed versions of these soils occur on imperfectly to poorly drained site locations. Three mineral soil types dominate the area (Figure 3.5): (1) Bridgewater type: a sandy, loam-sandy, clay-loam textured

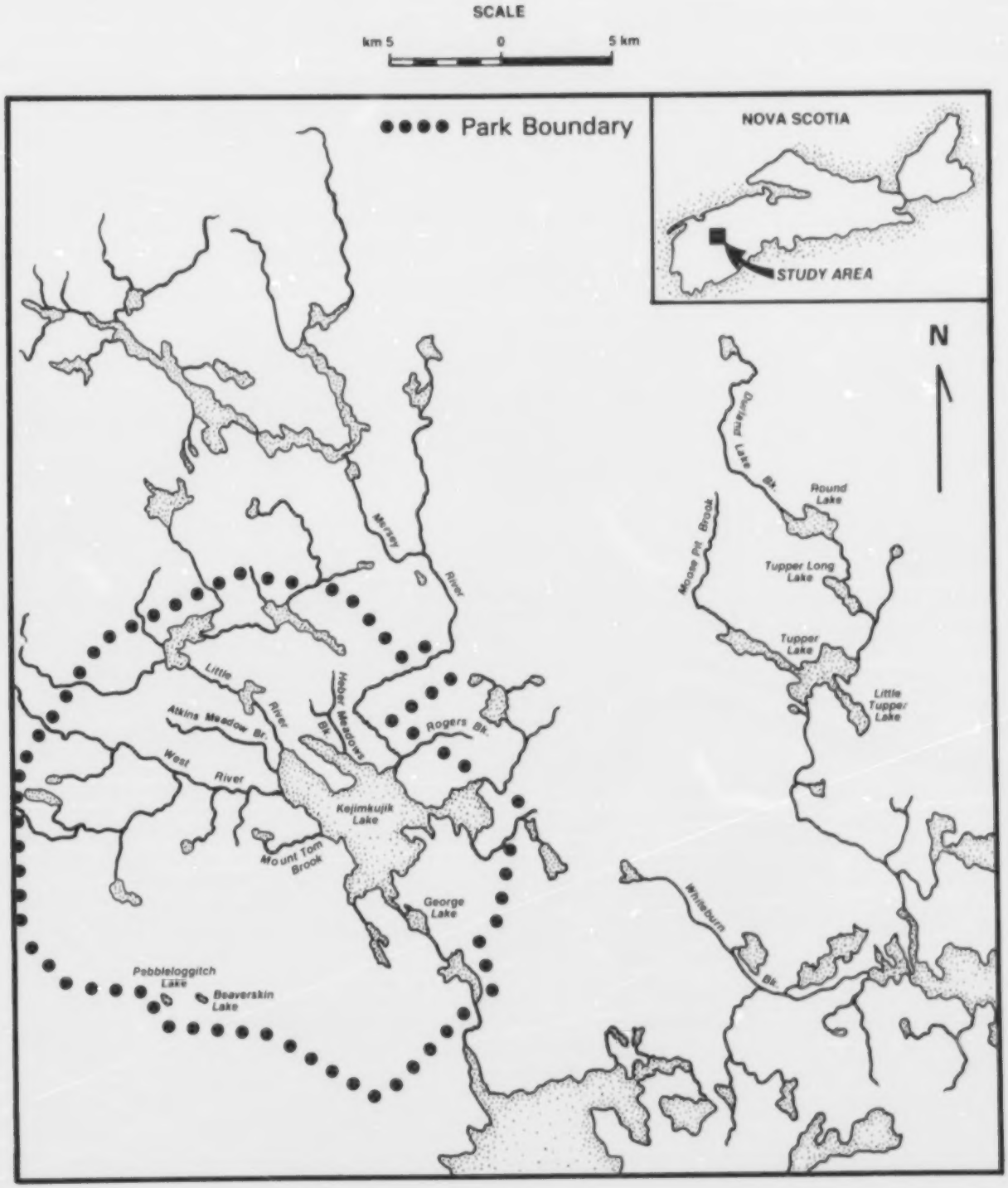


Figure 3.1. Location of Kejimkujik National Park.

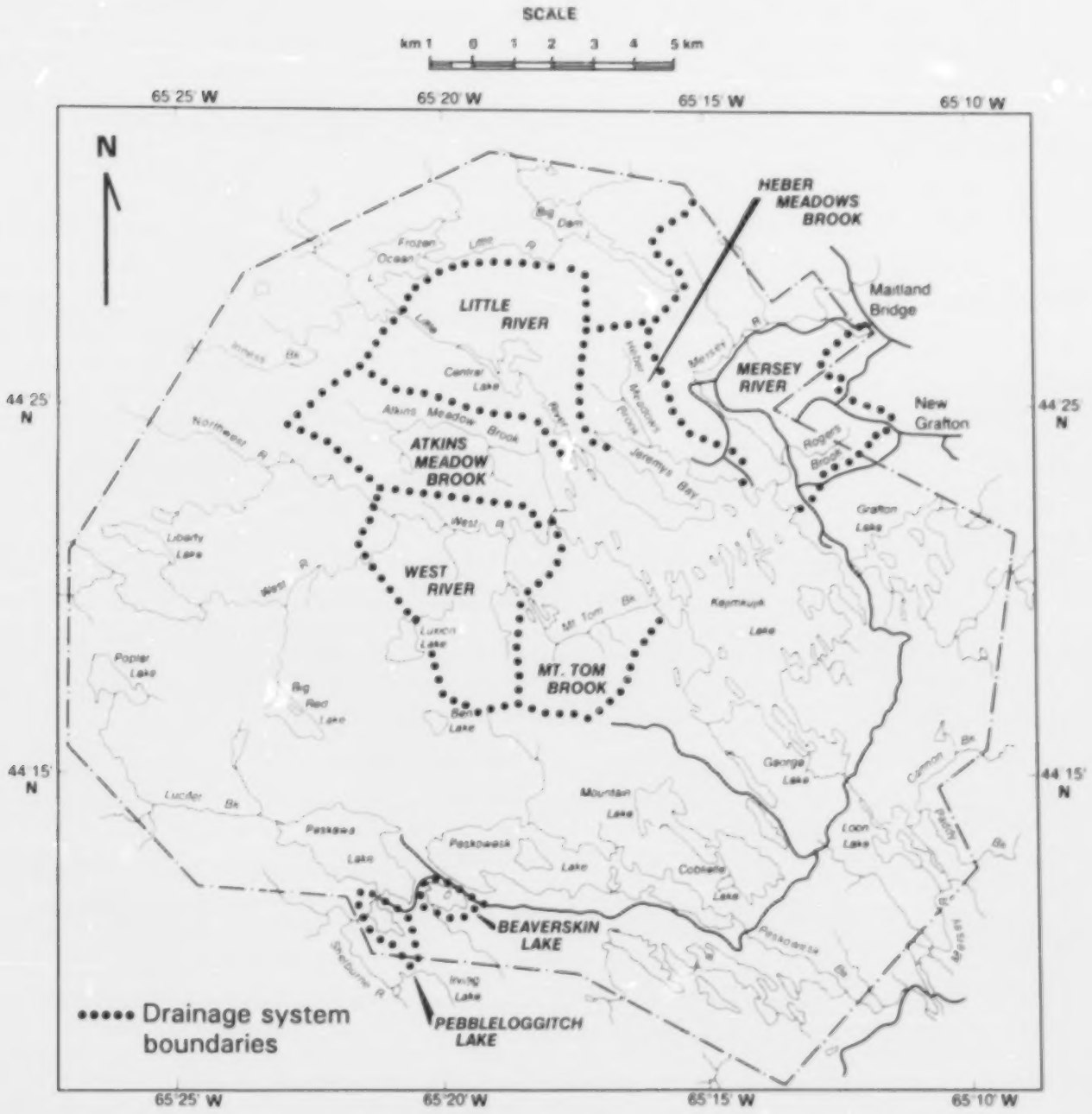


Figure 3.2. Location of drainage basins and sub-basins investigated in Kejimkujik National Park.

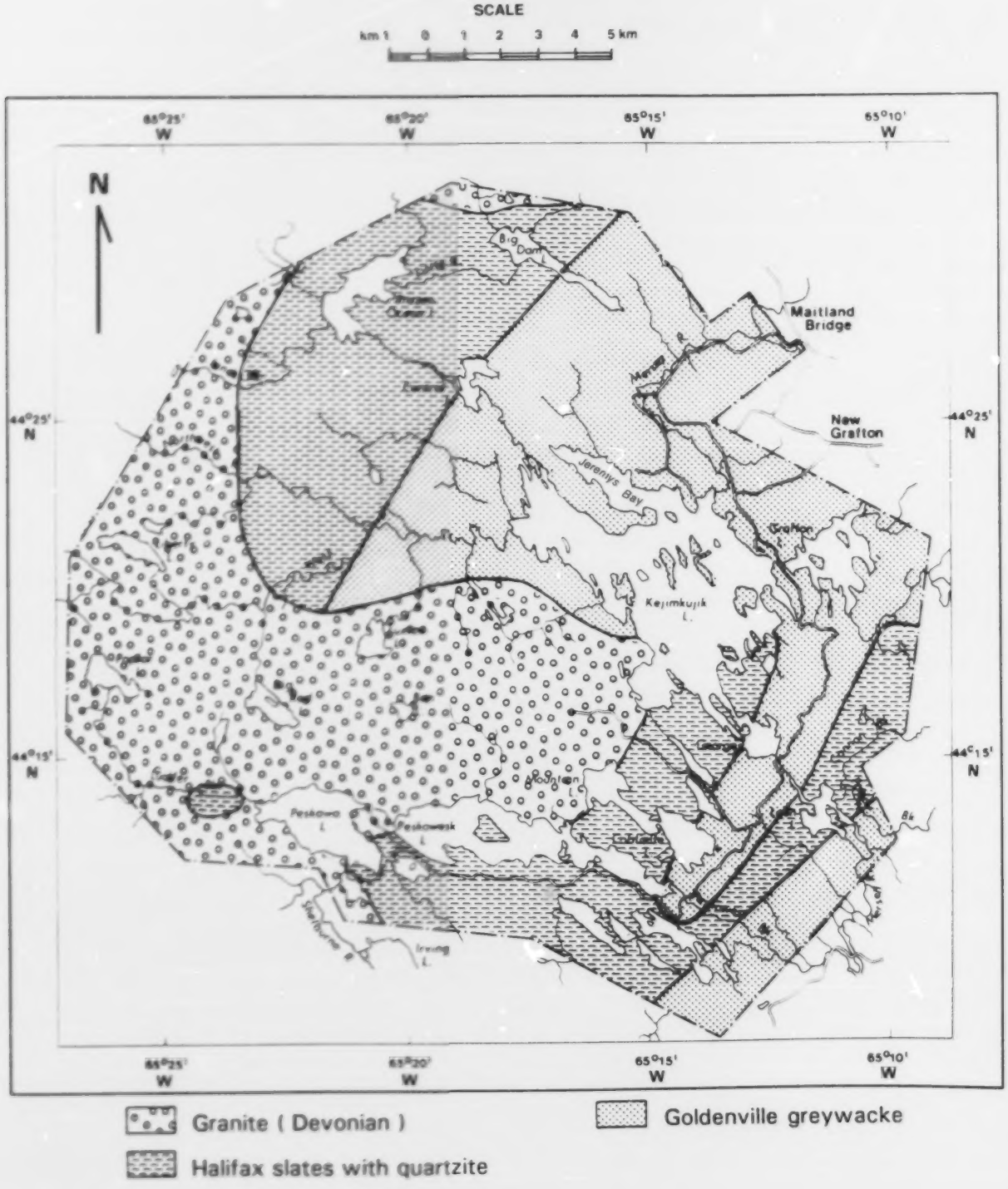


Figure 3.3. Bedrock geology in Kejimkujik National Park.

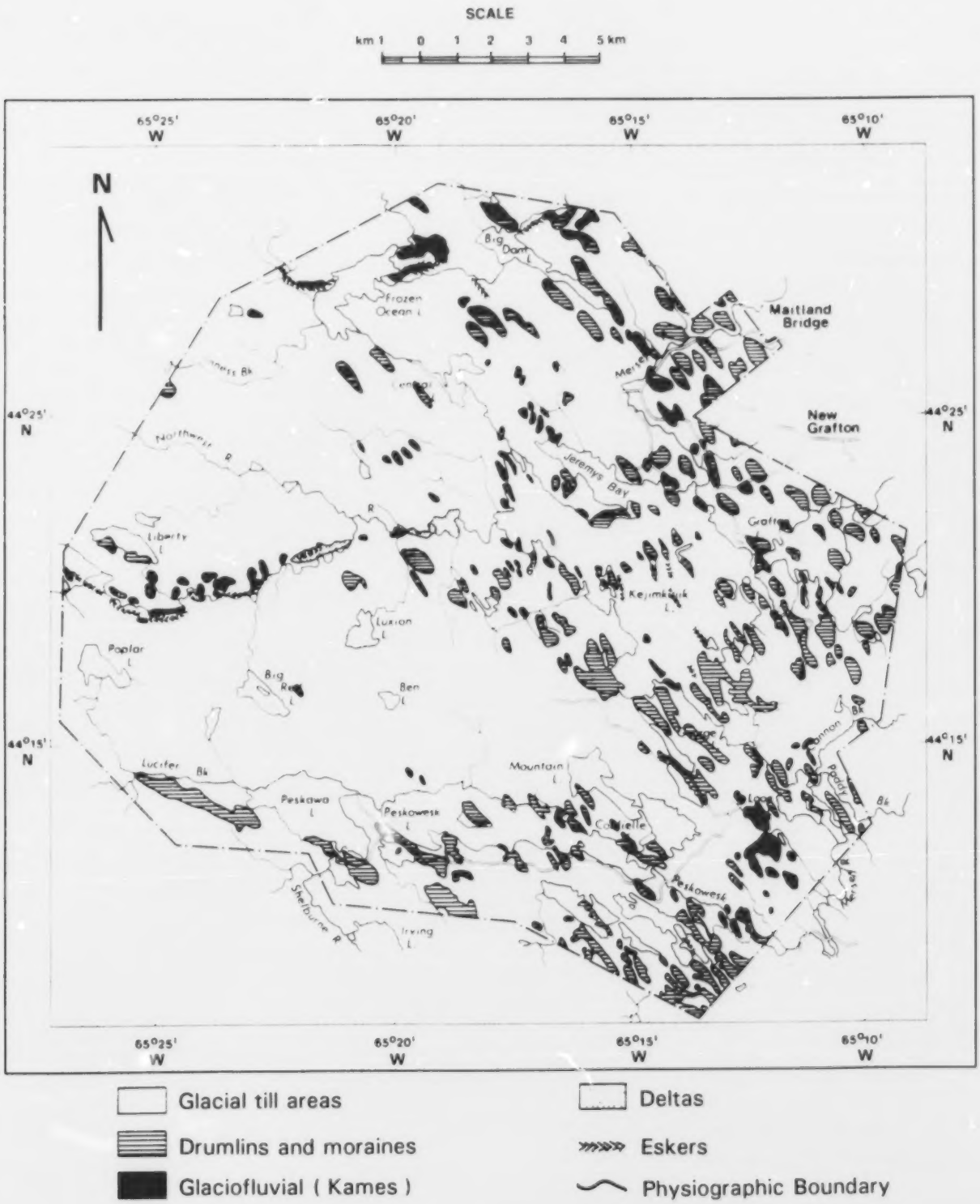


Figure 3.4. Landforms and surface deposits in Kejimkujik National Park.

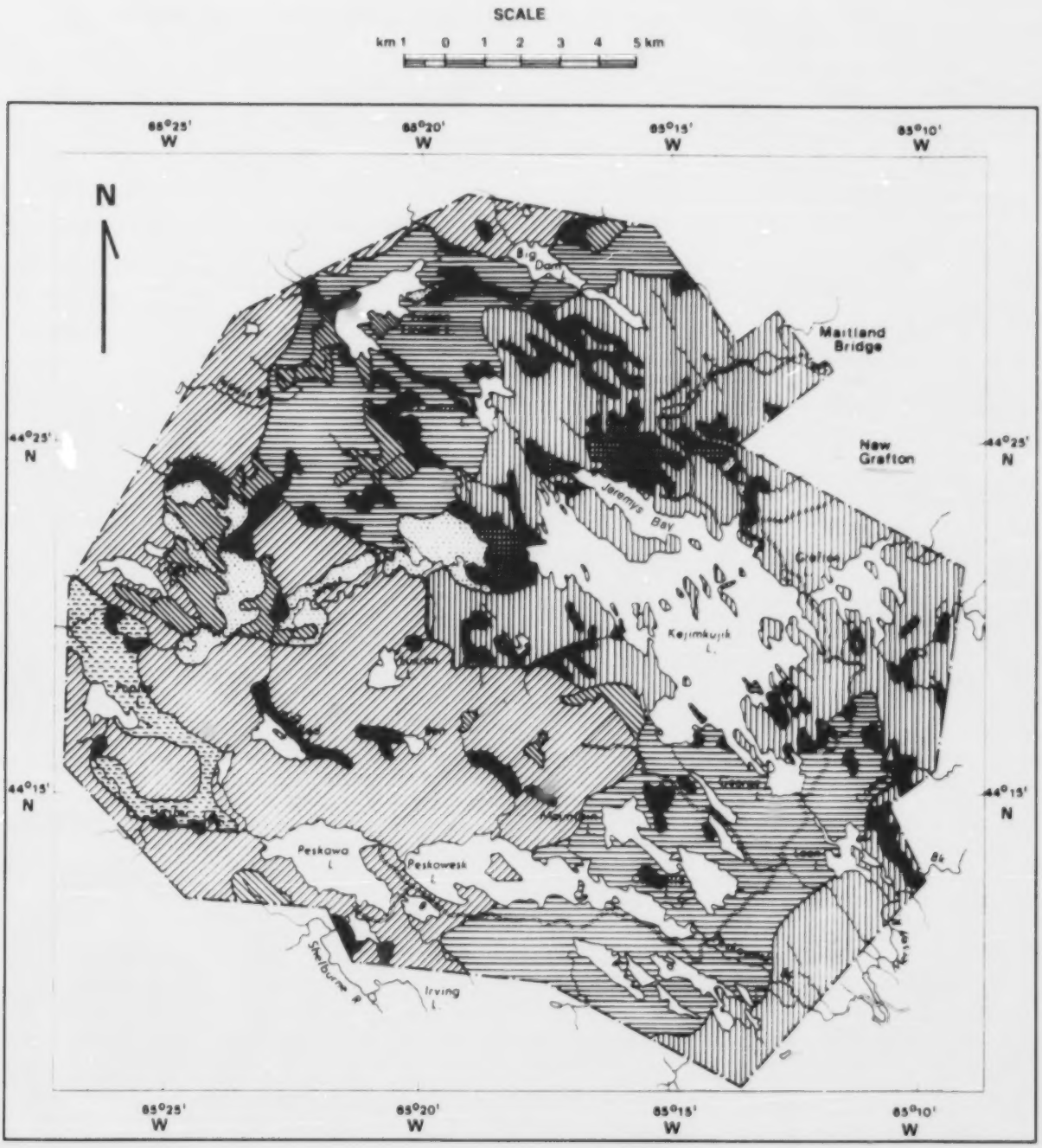


Figure 3.5. Soils in Kejimkujik National Park.

soil derived from medium textured glacial till; (2) Gibraltar type: a predominantly sandy loam textured material derived from moderately coarse textured granitic till. This soil is typically excessively stony and frequently shallow; (3) Halifax type: a well-drained excessively stony and cobbly sandy loam soil derived from moderately coarse textured till of slate and greywacke. Soils are generally nutrient poor and calcium deficient and are therefore highly susceptible to acidification. In addition, extensive peat deposits occur in shallow depressions along lacustrine and fluvial margins. These deposits occupy over 11% (3679 ha) of the total land surface area of the Park.

## 3.5 FOREST VEGETATION

Forest vegetation in the area is part of the Atlantic Uplands Section of the Acadian Forest Region (Rowe, 1972). The area is dominated by two major tree associations: "sugar maple - hemlock - pine" type and the "red spruce - hemlock - pine" type. The main tree associations are red maple (*Acer rubrum* L.), red oak (*Quercus borealis* Michx.), white birch (*Betula papyrifera* Marsh.), red spruce (*Picea rubens* Sarg.), eastern hemlock (*Tsuga canadensis* [L.] Carr.), balsam fir (*Abies balsamea* [L.] Mill.) and white pine (*Pinus strobus* L.). Approximately 75% of the forests are mixedwoods, 20% are softwoods and 5% are hardwoods (Gimbarzevsky, 1975). The forest cover is complex due to a high degree of disturbance throughout the area as a result of logging, fire and agricultural development. Insects and disease are the most important factors affecting the forests at present.

## 3.6 HYDROLOGIC CYCLE

Only two streams in the area have continuous discharge records (Howell, 1988). The Mersey River (Figure 4.1) has a surface area of 295 $km^2$ and is the highest order drainage system in the Park. A second stream Moose Pit Brook is a small low order stream with a surface area of 16.7 $km^2$ and is located a few kilometres outside of the Park boundaries. Both streams have similar hydrographs with maximum discharge at the end of March and a minimum at the end of September.

Howell (1988) has shown relationships between the hydrologic cycle in these drainage basins and ions associated with organic acidity (dissolved organic carbon) and ions associated with mineral acidity (sulphate). In the lower order basins, such as Moose Pit Brook, organic acidity appears to be inversely related to discharge, dominating in the late summer and autumn, while mineral acidity dominates in the winter and spring. Thus, the pH of these basins tends to remain relatively constant throughout the year. In higher order basins, such as Mersey River, there appears to be a response time lag of about three months in organic acidity which peaks only slightly in advance of the mineral acidity. This is attributed to "system water residence times" (Howell, 1989). The pH cycles annually, with maxima occurring in the late summer and minima in mid-winter.

# 4.0 WETLAND CLASSIFICATION AND VEGETATION

## 4.1 SAMPLING STRATEGY

Recent reviews on the role of wetlands in the acidification of surface waters (Environmental and Social Systems Analysts, 1986; Gorham *et al.*, 1984; Gorham *et al.*, 1986; Anderson, 1986) suggest that the type and position of wetlands in a catchment is important and that estimates of the percentage of the total catchment's drainage that passes through wetland areas might enhance the ability to interpret and predict the role of wetlands in basin water chemistry. It has been observed that this significance is further enhanced depending on the degree of isolation of the wetland from the regional water table. It was decided, therefore, that in this initial characterization of wetland vegetation, only those wetlands adjacent to surface waters (i.e. along fluvial and lacustrine margins) in the three basins would be sampled. It was further decided that emphasis would also focus on open fens and bogs, although a sufficient number of treed wetlands (e.g. hardwood swamps) would be sampled in order to provide a preliminary characterization of vegetation. The initial field survey was carried out by G. Wickware of Wickware and Associates, Inc., with C. Rubec and I. Kessel-Taylor of Environment Canada.

A total of 32 wetlands were sampled in the various basins and sub-basins within the Park in 1986. To facilitate sampling and future use of the data by monitoring agencies, wetlands within the Kejimkujik Lake basin were sampled from six sub-basins including Mersey River, Jeremys Bay, Little River, Atkins Meadow Brook, West River, and Mount Tom Brook. The locations of the 32 sampling sites are shown in Figure 4.1.

Maps showing the distribution, type and area of wetlands in each of the basins and sub-basins were prepared using existing 1:12 500 biophysical maps (Gimbarzevsky, 1975). Identified polygons were checked using 1:10 000 scale colour photography, and the physiognomic wetland type interpreted. The amount of area defined as wetland in this survey did not include all those imperfectly drained sites which may have 10-20 cm of surface organic layers - LFH layers under the Canadian System of Soil Classification (Canadian Soil Survey Committee, 1978), often with sphagnum moss, and whose leachate may have significant amounts of organic acids. These sites were not sampled during the 1986 reconnaissance program.

Collection of field data was carried out during August, 1986. During late summer, water levels in the study area are normally low. Unfortunately, 1986 was an extremely wet summer with all lakes and watercourses experiencing abnormally high water levels. Since most of the wetlands were located along lakeshore and fluvial systems margins, sampling, particularly for vegetation, was difficult. On many wetlands sampled, 0.5 to 1.0 m of water covered the site, except for the raised bogs and those wetlands not immediately connected hydrologically to a lake or fluvial system.

Using 1:10 000 colour aerial photographs, a representative selection of wetland types were identified in each of the basins and sub-basins for field sampling. Where possible (water depth permitting), a 10 m x 10 m rélevé plot was established in the dominant vegetation assemblage (condition) of each wetland. Where more than one assemblage was prevalent, two or more plots were established as required. Each plot was examined for species complement. Species were recorded on a standard field data collection form by height, stratum, and percent cover. Percent cover was visually estimated to the nearest 5 percent.

All sites described are classified according to their physiognomic character using the Canadian Wetland Classification System (National Wetlands Working Group, 1987). The location of the sites was also noted - i.e. adjacent to a lake (lacustrine), minor fluvial system (e.g. Mount Tom Brook, Atkins Meadow Brook), or major fluvial system (e.g. Little River, West River).

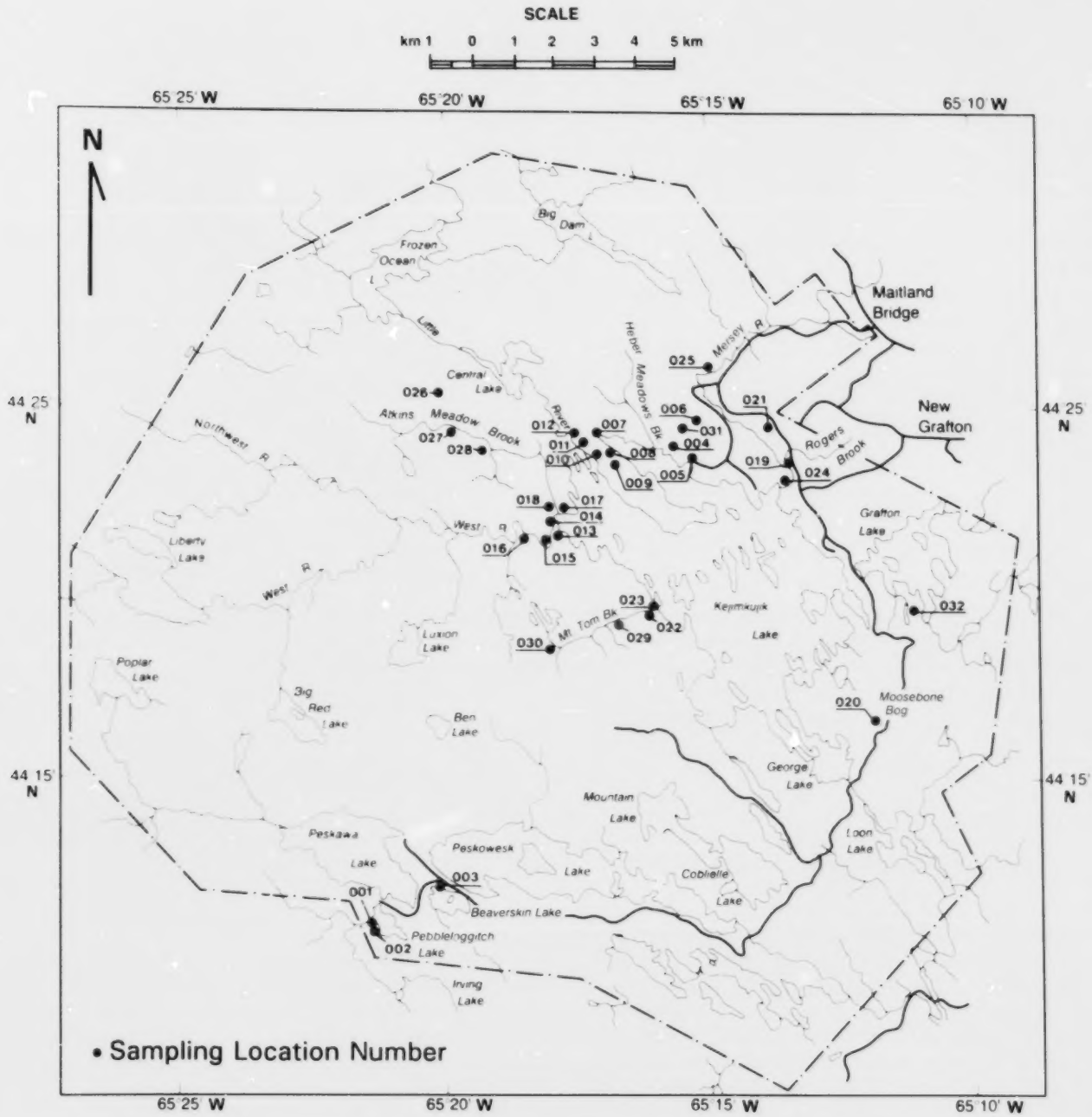


Figure 4.1. Wetland sampling locations in Kejimkujik National Park, 1986.

## 4.2 DISCUSSION

Wetlands in the Kejimkujik Lake basin and each of six sub-basins constitute significant proportions of basin area. Table 4.1 summarizes the estimated wetland area for each of the six sub-basins. The proportion of basin area occupied by wetlands ranges from 10% in the Mount Tom Brook sub-basin, to 31% in the Jeremys Bay sub-basin. Since the study area for these basins was limited to the area within Kejimkujik National Park, neither total basin area, nor percent area occupied by wetlands includes area external to the Park.

Comparative tables have been prepared to summarize vegetation (Table 4.2) for the various physiognomic wetland types and sub-basins within the Kejimkujik Lake basin of the LRTAP calibrated watershed. Extensive flooding on some sites during the sampling period in August, 1986 made it difficult to assess the vegetation complex at all sites and so the species list associated with Table 4.2 is incomplete. Only those species observed on site are included, usually those emergent above the water level.

### 4.2.1 *Swamps*

Hardwood swamps, typically recognized by a tree cover of red maple, are characterized by species such as *Chamaedaphne calyculata, Myrica gale, Acer rubrum, Carex stricta, Calamagrostis canadensis, Sphagnum angustifolium* and *Sphagnum palustre* (Table 4.2). These sites are typically found along fluvial margins adjacent to the upland site condition, in seepage zones and lower slope or bedrock depressions.

### 4.2.2 *Bogs*

Bogs of the watershed are associated with a range of site positions including lacustrine margins (usually low shrub bogs with slightly raised central areas and poor fen margins), in-filled lake basins or formerly shallow embayments of existing lakes (e.g. Heber Meadow) and poorly drained upland sites with acid soils. These latter sites are referred to as blanket bogs and often do not have depths of peat exceeding 40 cm. Vegetationally, bogs in this area are characterized by *Chamaedaphne calyculata, Kalmia angustifolium, Kalmia polifolia, Oxycoccos macrocarpon, Rhododendron canadense, Aronia prunifolia, Larix laricina* and distinctive moss and lichen components including *Sphagnum rubellum, Cladina mitis, Cladina stellaris*, and *Cladina rangiferina* (Table 4.2).

### 4.2.3 *Fens*

Fens are the most frequently occurring wetland class in the Park and are typically located along fluvial and lacustrine margins. Fens represent an intermediate stage in wetland succession and frequently develop from relatively nutrient-rich conditions and evolve to the nutrient-poor, ombrotrophic bog condition. Within this fen successional transition, two general physiognomic conditions may develop - a graminoid fen or shrub fen. Typically, although not necessarily, the graminoid phase is an early one, with the shrub phase developing later.

Graminoid fens in the study area are vegetationally characterized by a sparse cover of shrubs typically including *Spirea latifolia, Myrica gale* and *Alnus rugosa*. Graminoids, which frequently form dense swards, include *Carex stricta, Carex bullata* and *Calamagrostis canadensis*. *Osmunda regalis, Solidago* spp. and *Sphagnum angustifolium* also commonly occur (Table 4.2).

Shrub fens are characterized by a relatively continuous cover of shrubs which may either be very tall (2 to 4 m) or low (< 2 m). Low shrub fens are the most frequently occurring type and are characterized by *Chamaedaphne calyculata, Spirea latifolia, Myrica gale, Rhododendron canadense, Aronia prunifolia, Acer rubrum, Carex stricta* and *Sphagnum angustifolium* (Table 4.2).

## 4.3 SUMMARY

In the Kejimkujik Lake watershed, open peatlands may comprise up to 31% of the surface area of the various sub-basins. Bogs and fens are the major wetland classes encountered in the Kejimkujik area and have distinctive vegetational characteristics. Fens are the most common physiognomic type and frequently characterize the margins of most of the rivers in the area.

**Table 4.1. Summary of Estimated Wetland Area for Each of the Major Basins and Sub-basins.***

| BASIN/ SUB-BASIN NAME | OPEN WETLAND (ha) | TREED WETLAND (ha) | TOTAL WETLAND AREA (ha) | TOTAL AREA OF BASIN/ SUB-BASIN (ha) | PERCENT TOTAL WETLAND | PERCENT OPEN WETLAND | OPEN WETLAND PERCENT OF TOTAL WETLAND |
|---|---|---|---|---|---|---|---|
| Kejimkujik Basin | - | - | - | - | 16 | - | - |
| Sub-basins: | | | | | | | |
| Mersey River | 113 | 63 | 176 | 2965 | 6 | 4 | 67 |
| Heber Meadows Brook | 92 | 210 | 302 | 959 | 32 | 10 | 31 |
| Little River | 116 | 332 | 449 | 1480 | 30 | 8 | 27 |
| West River | 100 | 102 | 202 | 1762 | 11 | 6 | 55 |
| Atkins Meadow Brook | 164 | 148 | 312 | 1460 | 21 | 11 | 52 |
| Mount Tom Brook | 65 | 74 | 139 | 1375 | 10 | 5 | 50 |
| Pebbleloggitch Basin | 30 | - | 30 | 181 | - | 17 | - |
| Beaverskin Basin | - | 7 | 7 | 135 | 5 | - | - |

1 ha = 0.01 km$^2$

* Based on estimates of basin boundaries.

**Table 4.2. Summary of Vegetation Characteristics of Sites Sampled in the Kejimkujik LRTAP Watersheds.**

| SPECIES COMPLEMENT | BOGS | | | | FENS (Shrub) | | | | | FENS (Graminoid) | | | | SWAMPS | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Heber Meadows Brook | West River | Atkins Meadow Brook | Pebble-loggitch Lake | Heber Meadow Brook | Little River | West River | Mount Tom Brook | Atkins Meadow Brook | Mersey River | Mount Tom Brook | Little River | Atkins Meadow Brook | Heber Meadows Brook | Atkins Meadow Brook | Mount Tom Brook | Beaver -skin Lake |
| No. of Wetlands | 2 | 2 | 1 | 2 | 4 | 2 | 2 | 2 | 1 | 3 | 1 | 1 | 3 | 1 | 1 | 1 | 1 |
| **Trees** | | | | | | | | | | | | | | | | | |
| *Acer rubrum* | | | | | | | | | | | | | | x | x | x | x |
| *Pinus strobus* | | | | | | | | | | | | | | | | | |
| *Picea mariana* | | | | | | | | | | | | | | | | | |
| *Larix laricina* | | | | | | | | | | | | | | | | | |
| **Shrubs** | | | | | | | | | | | | | | | | | |
| *Chamaedaphne calyculata* | x | x | x | x | x | x | x | x | x | x | | | x | x | x | x | x |
| *Ledum groenlandicum* | x | | x | | | | | | x | | | | | | | | |
| *Kalmia angustifolium* | x | x | x | x | x | | x | | | | | | | | | | |
| *Kalmia polifolia* | x | x | x | x | | | | | x | | | | | | | | x |
| *Picea mariana* | x | x | | | | | | | | | | | | | | | |
| *Empetrum nigrum* | x | x | | | | | | | | x | | | | | | | |
| *Oxycoccos microcarpon* | x | | x | x | | | | | | | | | | | | | |
| *Gaylussacia baccata* | | x | x | | | | | | | | | | | | | | |
| *Vaccinium angustifolium* | x | | | | | | | | | x | x | x | x | | x | | |
| *Spirea latifolia* | | | | | x | x | x | x | | x | x | | x | x | x | | x |
| *Myrica gale* | | | | x | x | x | x | x | x | x | x | | x | | x | | |
| *Rhododendron canadense* | | x | x | x | x | x | x | x | x | | | | | x | | | |
| *Aronia prunifolia* | x | x | x | x | x | x | x | x | x | | | | | | | x | |
| *Larix laricina* | x | x | x | | | | | | | | x | | x | | | | |
| *Alnus rugosa* | | | | | x | x | | x | | x | | | | | | x | x |
| *Acer rubrum* | | | | | | x | | x | | x | | x | | | | | x |
| *Oxycoccos macrocarpon* | | | | x | | | | | | | | | | | | | |
| *Pinus strobus* | x | x | x | | | | | | | | | | | | | | |
| *Viburnum cassinoides* | | | | | | | | | | | | | | | | | |
| *Andromeda glaucophylla* | | | | | | | | | | | | | | | | | |
| *Gaultheria procumbens* | | | x | | | | | | | | | | | | | x | |
| *Sorbus decora* | | | | | | | | | | | | | | | | | |
| **Herbs** | | | | | | | | | | | | | | | | | |
| *Coptis trifolia* | | x | x | | | | | | | | | | | | x | | |
| *Solidago spp.* | x | | x | | | | | | | | | | | | | | |
| *Lysimachia terrestris* | | | | | x | | | | | x | | | x | | | x | |
| *Iris versicolor* | | | | | x | | | | | | | | | | | | |
| *Drosera rotundifolia* | | | | | | | | | | | x | | | | | x | |
| *Lucopus uniflora* | | | | | | | | x | | | | | | | | | x |
| *Sarracenia purpurea* | x | | | x | | | | | | | | | | | | | x |
| *Trientalis borealis* | | | | | | | | | | | | | | | | | x |
| *Mitella nuda* | | | | | | | | | | | | | | | | | x |
| *Mitchelia repens* | | | | | | | | | | | | | | x | | x | x |
| *Osmunda cinnamonea* | | | | | | | | | | | | | | | | | x |
| *Mianthenum canadense* | | | | | | | | x | | x | x | | | | | | |
| *Aster spp.* | | | | | | x | | | | | | x | | | | | |
| *Osmunda regalis* | | | | | | x | | | | | | | | | | | |
| *Woodwardii virginica* | | | | | | | | | | | | | | | | | |
| *Rubus chamaemorous* | | x | | | | | | | | | | | | | | | |

**Table 4.2. (Continued)**

| SPECIES COMPLEMENT | BOGS | | | | FENS (Shrub) | | | | | FENS (Graminoid) | | | | SWAMPS | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Heber Meadows Brook | West River | Atkins Meadow Brook | Pebble-loggitch Lake | Heber Meadows Brook | Little River | West River | Mount Tom Brook | Atkins Meadow Brook | Mersey River | Mount Tom Brook | Little River | Atkins Meadow Brook | Heber Meadows Brook | Atkins Meadow Brook | Mount Tom Brook | Beaver -skin Lake |
| No. of Wetlands | 2 | 2 | 1 | 2 | 4 | 2 | 2 | 2 | 1 | 3 | 1 | 1 | 3 | 1 | 1 | 1 | 1 |
| **Herbs (continued)** | | | | | | | | | | | | | | | | | |
| *Rhus radicans* | | | | | | | | | | | | | | | | x | |
| *Thelypteris palustris* | | | | | | | | | | | | | | | | x | |
| *Hypericum virginicum* | | | | | x | | | | | | | | | | | | |
| *Smilacina trifolia* | | | | | | | | | | | | | | | | | x |
| **Graminoids** | | | | | | | | | | | | | | | | | |
| *Carex stricta* | | x | x | | x | x | x | x | x | x | x | x | x | x | x | x | |
| *Carex rostrata* | | | | | x | x | | x | | | | x | | | | | |
| *Carex aquatilis* | | | | | | | | | | | | | | | | | |
| *Carex bullata* | | | | | x | | | | | x | x | x | x | | | | |
| *Carex oligosperma* | | x | | x | x | | | | | | | | | | | | |
| *Calamagrostis canadensis* | | | | | | x | x | | | x | x | x | x | x | x | x | |
| *Calamagrostis neglecta* | | | | | | | | x | | | | | | | | | |
| *Dulichium arundinaccum* | | | | | x | | | | | | | | | | | | |
| *Rhyncospora alba* | | x | | | | | | | | | | | | | | | |
| *Scirpus caespitosus* | | x | | x | | | | | | | | | | | | | |
| *Eriophorum virginicum* | | | | | | | | | | | | | | | | | |
| *Spartina pectinata* | | | | | | | | | | x | | | | | | | |
| *Carex trisperma* | | | | | | | | | | | | | | | | | x |
| *Eriophosum spissum* | | | | | | | | | | | | | | | | | |
| *Gleyceria canadensis* | | | | | | | | | | | | | | | | | |
| **Mosses and lichens** | | | | | | | | | | | | | | | | | |
| *Sphagnum fuscum* | x | | x | | | | | | | | | | | | | | |
| *Sphagnum rubellum* | x | x | x | x | | | | | | | | | | | | | |
| *Sphagnum angustifolium* | x | | | x | x | x | x | | x | x | x | | x | x | x | | |
| *Sphagnum palustre* | | x | | | | | | x | | | | | | | x | x | |
| *Sphagnum magellanicum* | x | | | | | | | | | | | | | | | | x |
| *Sphagnum girgensohnii* | | | | | | | | | | | | | | | x | | |
| *Sphagnum torreyanum* | | | | | | | | x | | | | | | | | | |
| *Cladina mitis* | x | x | x | | | | | | | | | | | | | | |
| *Cladina stellaris* | x | x | x | | | | | | | | | | | | | | |
| *Cladina uncialis* | | x | x | | | | | | | | | | | | | | |
| *Cladina rangiferina* | x | x | x | x | | | | | | | | | | | | | |
| *Sphagnum nemoreum* | | | | x | | | | | | | | | | | | | x |
| *Dicranum scoparium* | | | | | | | | | | | | | | | | | x |
| *Polytrichum commune* | x | | | | | | | | | | | | | | | | |
| *Dicranum* spp. | | | | | | | | | | | | | | | x | | |
| *Mnium* spp. | | | | x | | | | | | | | | | | | | |

# 5.0 SEASONAL AND VEGETATIONAL EFFECTS ON WETLAND CHEMISTRY

## 5.1 SAMPLING AND METHODS

The second phase of the program addressed the questions of whether there is a seasonal aspect to wetland soil chemistry, as well as whether the dominant wetland classes in the Park (bogs and fens) can be distinguished chemically.

Soil and water sampling were carried out on eight wetlands in six sub-basins of the Kejimkujik Lake drainage basin. The sub-basins included: Little River, Mersey River, Atkins Meadow Brook, Heber Meadows Brook, Rogers Brook and West River (Figure 5.1). One wetland was sampled within each sub-basin, with the exception of West River and Heber Meadows Brook, in which sampling was done at two locations. All of the wetlands sampled were open (non-treed). Of the wetlands surveyed, three were bogs (Heber Meadows Brook, Atkins Meadow Brook and a site near the mouth of West River) and the remaining four were classified as graminoid and shrub fens (Wickware, 1987). The oligotrophic nature of the bogs was indicated visually by a dense carpet of sphagnum vegetation, while the fens were generally recognized by the predominance of *Carex* species. Water and peat sampling was repeated at the same sites during each of three field visits in 1987.

Collection of field data was carried out on May 19, September 14 and November 24, 1987. These dates were chosen to coincide approximately with maxima or minima in sulphate ($SO_4$) and dissolved organic carbon (DOC) concentrations in the streamwater. Howell (1988) reports maximum $SO_4$ concentrations in the streamwater in the spring flood season, followed by a minimum in the late summer, increasing again in the late autumn. DOC tends to follow an opposing cycle, with minima in the spring and late autumn and a maximum in the late summer.

Two 2.5-cm-diameter peat cores spaced 1 m apart were removed from the top 50 cm of each wetland sampling site. Two peat cores per site were taken to provide some indication of the variance of the peat chemistry at each site. The sites were generally located within about 30 m of the adjacent river or stream, into which mobile water from the peat was still likely to drain rather than evaporate, as might occur further inland. In the case of Heber Meadows Brook (Figure 5.1), peat cores were removed from two sites (two cores per site), one site located within 20 m and a second site about 200 m from the Brook.

Peat samples were later homogenized in a blender in the laboratory and the pH was determined by a glass electrode in contact with the peat, allowing 30 to 60 minutes for the reading to stabilize. The samples were then air dried, homogenized again and washed with hydrochloric acid (HCl) and barium acetate $Ba(OAc)_2$. Cation exchange capacity was determined by titration. Total carbon (C) of the air-dried sample was determined by a Leco carbon analyzer and total nitrogen (N) by the Kjeldhal procedure. Following this, the sample was oven dried, ashed at 550°C and digested with $HCl-HClO_4$ (hydrochloric acid - hydriotic acid). Concentrations of aluminum (Al), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na) and phosphorus (K) were analyzed by atomic absorption spectrophotometry, and chlorine (Cl) and $SO_4$ by ion chromatography.

Streamwater samples were taken from locations a few metres upstream and also downstream from each sampling station. Water samples were analyzed for colour and ionic constituents. The pH was determined using a glass electrode, Al, Fe, Ca and Mg were measured by atomic absorption spectrophotometry, Na and K by flame photometry, and $SO_4$ and Cl by ion chromatography. The colour was determined against a platinum - cobalt (Pt-Co) standard. Total N was determined colorimetrically, Gran alkalinity by titration, and DOC by ultraviolet (UV) digestion and colorimetry. Organic anions were computed using the method of Oliver *et al.* (1983).

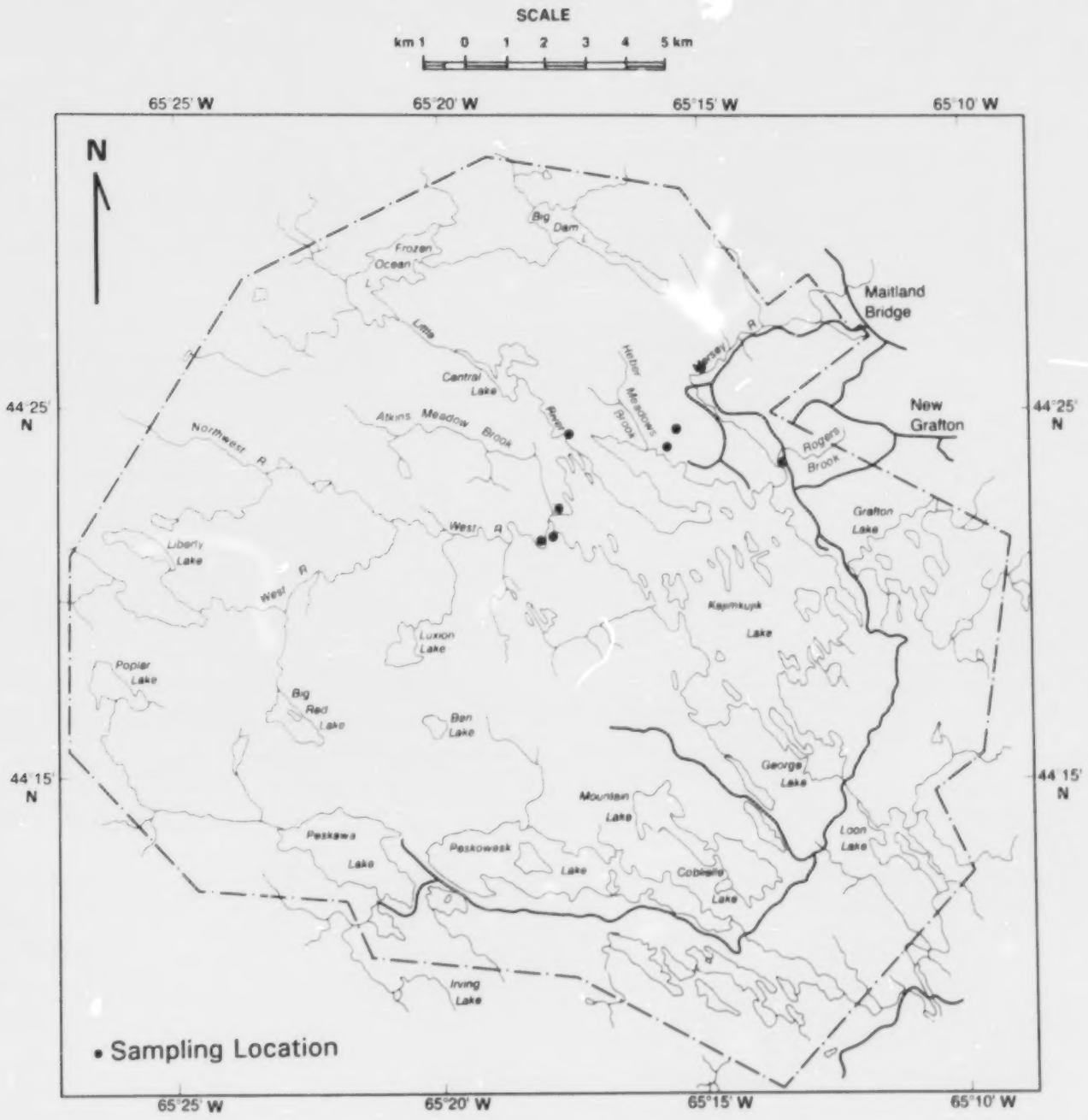


Figure 5.1 Wetland sampling locations in Kejimkujik National Park, 1987.

## 5.2 ANALYTICAL METHODOLOGY

Ionic constituents for the peat (usually two cores for each wetland) and water were averaged to obtain a single value for each wetland in each season. Since there was a wide variance in the parameters between the different wetlands, averaged peat and water data were then transformed to the $\log_e$ scale to reduce the variance. This transformation was applied to all of the chemical parameters except the pH, colour, alkalinity and ash content in the peat chemistry data, and the pH, colour, conductivity, turbidity, alkalinity, and total cations and anions for the water chemistry data. These were not transformed owing to the relatively narrow scatter of the data. Plots were then prepared for all of the chemical parameters showing the size and nature of the seasonal changes.

Outlier data were identified visually and eliminated to avoid a skewed distribution. Tables were produced showing seasonal mean values for each chemical parameter for all seven wetlands (Tables 5.1 and 5.2). Wetlands were subdivided into two classes (Tables 5.3 and 5.4) on the basis of national wetland classification standards (National Wetlands Working Group, 1987): bogs, which are dominated by sphagnum vegetation and, being essentially oligotrophic, receive much of their nutrients from rainwater; and fens, which are more eutrophic in character and dominated by *Carex* species.

For each variable in the two media (peat and streamwater) a pair-wise comparison was made between seasons for all of the wetlands. This permitted determination of the occurrence of significant seasonal differences.

Significance levels (probabilities) were determined for F-values, generated by a two-level factorial analysis of variance (ANOVA) procedure using SAS GLM (Joyner, 1985), for a crossed design (wetland versus season), with correction for unequal weighting as described in Snedecor and Cochran (1967). The data were unequally weighted because, in a few instances, only a single peat core was collected from a wetland, rather than a pair, which skews the distribution of data. A correction procedure is required to normalize for this (Snedecor and Cochran, 1967). The probability that the difference occurred randomly between any two seasons is grouped into three significance levels: 0.10, 0.05 and 0.01 (Tables 5.1 and 5.2). For the peat and the streamwater, there were three such comparisons per parameter, May versus September, May versus November, and September versus November.

Analysis of variance was also carried out for each variable to test for the difference between bogs and fens. Significance levels were again determined by an F-test, as above. In this case, however, the design was nested instead of crossed. There were two levels of nesting: individual samples (two per wetland) nested within wetlands, and individual wetlands nested within the wetland class (bog or fen). The probability of a randomly occurring difference in any of the chemical parameters between bogs and fens was categorized into two levels of significance: 0.10 and 0.05 (Tables 5.1 and 5.2). Significance levels are not available for the annual means owing to theoretical difficulties involved in their determination.

The individual variability in peat chemistry is important because of the relatively small sample size, both of individual peat cores (14 samples) and also of wetlands (7 sites). If the variance between pairs of parallel peat cores (1 m apart) in each wetland exceeds the variance between wetlands for a particular chemical parameter, then the difference between seasonal changes or between wetland classes (bogs and fens) will not be significant. In Tables 5.1 to 5.4, many of the differences between seasons, as well as between wetland classes (bogs versus fens), were not significant (i.e. $p>0.10$). In most cases, this is due to a high variance between wetlands rather than the variance between parallel peat cores within each wetland. Individual sample variance within each wetland was relatively low. This is demonstrated in Table 5.5 in which F-values for each chemical parameter were computed for the peat by a one-way ANOVA procedure using SAS GLM (Joyner, 1985).

The F-values (Table 5.5) are the ratio of the mean square of each chemical parameter for the individual peat cores in each wetland, to the mean square for all wetlands. Probabilities of a random occurrence (significance levels) are also listed. At F = 1, the probability is 0.50. As F becomes larger, the probability decreases toward zero. At the p = 0.05 level of significance, the F-value generally ranges between 3 and 4.

Most of the F-values in Table 5.5 are relatively high ($F > 4$) and the probabilities low ($p < 0.05$), indicating that the variance in chemistry within each wetland (i.e. between parallel peat cores) was much lower than the variance between wetlands. Thus, in Tables 5.1 to 5.4, "between" wetland variability and not "within" wetland variability was generally responsible for most of the cases where seasonal differences or differences between wetland classes were not significant.

## 5.3 RESULTS

Concentrations of hydrogen (H), Al, Fe, Ca, Mg, Na, K, $SO_4$ and Cl in the peat are expressed in $mg \cdot g^{-1}$ and in the streamwater are expressed in $mg \cdot L^{-1}$ (Tables 5.1 to 5.4). These units for the peat are convenient because peat chemistry cannot be expressed on a volume basis. Organic anions in the water are reported in $meq \cdot L^{-1}$. Ash contents and C and N values of the peat are expressed in percent (%) dry weight. The cation exchange capacity (CEC) is given in meq/100 g dry weight of soil.

Ion balances in the streamwater (i.e. total cations - total anions / total cations + total anions) were within the 10% range of acceptable variability (Howell, personal communication). For the peat, cations and anions do not need to be balanced, instead being balanced by the soil colloidal material. The much larger number of cations reflects the dominantly negative charge of the organic colloids.

## 5.4 SEASONAL CHANGES

Significant seasonal changes occurred for some aspects of the peat chemistry including Na, K, Mg, Ca, Fe, Al, H, C and N concentrations, as well as the CEC and the C/N ratio (Table 5.1), but only for some seasons and not all, except C, N and C/N. Significant changes were particularly numerous between May and November suggesting an annual cycling in these constituents (from spring to autumn) rather than a biannual (e.g. spring - summer - autumn) cycle. Cycling may be related to seasonal changes in H, which in turn is related to the hydrologic cycle (water table changes) which affects organic acid production. It is well known that the solubility of Al and Fe is highly dependent on the pH (Shotyk, 1988). The CEC of organic colloids is also highly pH dependent (Stevenson, 1982). As the pH declines from May to November, Al levels appear to decrease. However, Fe and CEC both increase - the opposite of the expected trend, suggesting that other factors are having an over-riding influence here.

Between May and November, H in the peat increased considerably. This was accompanied by a similar and expected H increase in the streamwater during the same period (Table 5.2). The increase in H in the streamwater is accompanied by a significant decline in alkalinity during the same period. The increase in H in the streamwater between May and November also corresponds to a significant increase in organic anions during this period. A significant fluctuation in $SO_4$ levels in the soil was anticipated. Sulphate storage in wetlands often fluctuates as a result of oxidation and flushing of sulphur associated with seasonal fluctuations in the water table (Bayley *et al.*, 1986). However, $SO_4$ did not show any significant seasonal trend in the peat, although there was a significant increase in the streamwater from May to November. The acidity balance of the peat appears to be controlled mainly by C/N ratios regulating the production of organic anions, rather than by $SO_4$, whereas the acidity of the streamwater is controlled by both organic and mineral anions. Howell (1988) and Kerekes *et al.* (1986) also found that the acidity in the streams of the Kejimkujik area are controlled by both types of ions.

**Table 5.1. Peat Chemistry: Seasonal Means ****

| | May | SE | MS | Sept | SE | SN | Nov | SE | MN |
|---|---|---|---|---|---|---|---|---|---|
| pH | 3.51 | 3 | * | 3.33 | 3 | - | 3.26 | 4 | * |
| H mg·L$^{-1}$ | 0.31 | 3 | * | 0.47 | 3 | - | 0.55 | 4 | * |
| Al | 14.00 | 28 | - | 12.73 | 25 | - | 11.26 | 21 | # |
| Fe | 2.56 | 30 | - | 2.02 | 15 | * | 4.93 | 15 | * |
| Ca | 0.15 | 31 | @ | 0.31 | 33 | - | 0.32 | 17 | * |
| Mg | 0.63 | 30 | - | 0.40 | 13 | # | 0.35 | 20 | # |
| Na | 2.85 | 20 | * | 0.41 | 28 | - | 0.37 | 18 | # |
| K | 2.32 | 27 | @ | 1.11 | 27 | - | 1.29 | 27 | * |
| $SO_4$ | 0.88 | 23 | - | 0.80 | 21 | - | 0.87 | 18 | - |
| Cl | 0.14 | 10 | - | 0.03 | 29 | * | 0.30 | 32 | - |
| Total C % | 43.14 | 15 | @ | 45.33 | 9 | @ | 38.34 | 14 | # |
| Total N % | 1.49 | 12 | @ | 1.83 | 8 | @ | 1.78 | 7 | @ |
| C/N | 28.93 | 22 | @ | 24.75 | 13 | # | 21.52 | 15 | # |
| CEC meq/100 g | 82.33 | 11 | - | 76.05 | 8 | @ | 97.23 | 10 | * |
| Totals: | | | | | | | | | |
| Anions meq·g$^{-1}$ | 0.02 | 24 | - | 0.02 | 20 | - | 0.03 | 21 | - |
| Cations meq·g$^{-1}$ | 1.94 | 20 | - | 1.62 | 23 | - | 1.61 | 18 | - |

SE = Standard Error of the Mean, %

Seasonal Changes:

MS = May - September
SN = September - November
MN = May - November

Differences in seasonal mean (Tables 5.1 and 5.2) significant at:

@ $p < 0.10$
# $p < 0.05$
* $p > 0.01$

** 8 wetlands, 14 samples. All units in mg·g$^{-1}$ except as otherwise indicated

**Table 5.2. Streamwater Chemistry: Seasonal Means****

| | May | SE | MS | Sept | SE | SN | Nov | SE | MN |
|---|---|---|---|---|---|---|---|---|---|
| pH | 4.84 | 4 | * | 5.48 | 4 | * | 4.43 | 2 | # |
| H | 0.15 | 4 | * | 0.003 | 4 | * | 0.037 | 2 | * |
| Al | 0.16 | 15 | - | 0.14 | 10 | # | 0.27 | 15 | * |
| Fe | 0.23 | 13 | * | 0.81 | 24 | # | 0.37 | 11 | * |
| Ca | 0.45 | 12 | # | 0.66 | 17 | | 0.77 | 12 | * |
| Mg | 0.33 | 7 | * | 0.49 | 10 | # | 0.60 | 6 | * |
| Na | 2.70 | 4 | * | 3.59 | 4 | - | 3.29 | 3 | * |
| K | 0.21 | 8 | # | 0.50 | 22 | # | 0.17 | 13 | * |
| $SO_4$ | 1.91 | 7 | - | 2.87 | 22 | - | 3.75 | 10 | * |
| Cl | 3.82 | 5 | * | 4.98 | 4 | * | 4.09 | 4 | * |
| DOC | 9.04 | 7 | - | 7.71 | 18 | * | 17.50 | 7 | * |
| N | 0.10 | 1 | - | 0.16 | 11 | - | 0.10 | 2 | - |
| Org. Anions meq·L$^{-1}$ | 63.3 | 7 | - | 62.2 | 18 | * | 110.0 | 7 | * |
| Gran Alk. mg·L$^{-1}$ | -0.84 | 67 | # | -0.95 | 45 | * | -2.24 | 22 | * |
| Totals: | | | | | | | | | |
| Anions meq·L$^{-1}$ | 0.22 | 4 | * | 0.29 | 6 | - | 0.30 | 4 | * |
| Cations meq·L$^{-1}$ | 0.20 | 3 | * | 0.27 | 8 | * | 0.28 | 2 | * |

SE = Standard Error of the Mean, %

Seasonal Changes:

MS = May - September
SN = September - November
MN = May - November

Differences in seasonal mean (Tables 5.1 and 5.2) significant at:

@ $p < 0.10$
# $p < 0.05$
* $p > 0.01$

** 8 wetlands, 14 samples. All units in mg·L$^{-1}$ except as otherwise indicated.

**Table 5.3. Peat Chemistry: Seasonal and Annual Means for Bogs vs Fens***

| | May | | | Sept | | | Nov | | | Annual Mean ** | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Bog | Fen | | Bog | Fen | | Bog | Fen | | Bog | Fen |
| pH | 3.24 | 3.68 | # | 3.02 | 3.51 | # | 2.86 | 3.50 | # | 3.04 | 3.56 |
| H | 0.575 | 0.209 | # | 0.955 | 0.309 | # | 1.380 | 0.316 | # | 0.912 | 0.275 |
| Al | 17.92 | 17.65 | @ | 5.66 | 16.96 | # | 5.00 | 15.01 | @ | 6.20 | 16.54 |
| Fe | 1.62 | 3.12 | @ | 1.28 | 2.46 | # | 4.58 | 5.14 | - | 2.49 | 3.57 |
| Ca | 0.09 | 0.19 | - | 0.16 | 0.40 | - | 0.25 | 0.35 | - | 0.17 | 0.32 |
| Mg | 0.57 | 0.67 | - | 0.42 | 0.39 | - | 0.39 | 0.32 | - | 0.46 | 0.46 |
| Na | 2.03 | 3.34 | @ | 0.21 | 0.52 | @ | 0.22 | 0.46 | @ | 0.82 | 1.44 |
| K | 1.52 | 2.82 | @ | 0.69 | 1.36 | @ | 0.48 | 1.78 | @ | 0.89 | 1.98 |
| $SO_4$ | 1.04 | 0.79 | - | 0.64 | 0.90 | - | 0.69 | 0.98 | - | 0.79 | 0.89 |
| Cl | 0.24 | 0.08 | - | 0.02 | 0.03 | - | 0.19 | 0.25 | - | 0.15 | 0.12 |
| Total C % | 56.33 | 35.23 | # | 51.53 | 41.61 | @ | 51.67 | 30.35 | # | 53.14 | 35.73 |
| Total N % | 1.22 | 1.66 | - | 1.48 | 2.04 | - | 1.68 | 1.83 | - | 1.46 | 1.84 |
| C/N | 50.44 | 22.84 | # | 35.94 | 20.21 | # | 31.42 | 16.67 | # | 39.27 | 19.91 |
| Ash % | 21.71 | 44.31 | @ | 15.54 | 36.26 | @ | 15.26 | 46.98 | @ | 17.50 | 42.52 |
| CEC: meq/100 g | 97.87 | 73.01 | - | 73.52 | 77.57 | - | 120.12 | 83.50 | - | 97.17 | 78.02 |
| Totals: | | | | | | | | | | | |
| Anions meq·g$^{-1}$ | 0.03 | 0.02 | - | 0.01 | 0.02 | - | 0.02 | 0.03 | - | 0.02 | 0.02 |
| Cations meq·g$^{-1}$ | 1.15 | 2.41 | @ | 0.77 | 2.13 | @ | 0.87 | 2.06 | @ | 0.93 | 2.20 |

Differences between bog and fen means (Tables 5.3 and 5.4) significant at:
@ $p < 0.10$
# $p < 0.05$

* All units in mg·g$^{-1}$ except as otherwise indicated
** Significance levels of annual means not available

**Table 5.4. Streamwater Chemistry: Seasonal and Annual Means for Bogs vs Fens***

| | May | | | Sept | | | Nov | | | Annual Mean ** | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Bog | Fen | | Bog | Fen | | Bog | Fen | | Bog | Fen |
| pH | 4.45 | 4.99 | - | 5.45 | 5.49 | - | 4.25 | 4.50 | - | 4.72 | 4.99 |
| H | 0.035 | 0.010 | - | 0.004 | 0.003 | - | 0.056 | 0.32 | - | 0.019 | 0.010 |
| Al | 0.15 | 0.16 | - | 0.19 | 0.12 | - | 0.27 | 0.28 | - | 0.21 | 0.18 |
| Fe | 0.22 | 0.23 | - | 0.86 | 0.78 | - | 0.36 | 0.38 | - | 0.49 | 0.47 |
| Ca | 0.36 | 0.49 | - | 0.55 | 0.70 | - | 0.61 | 0.84 | - | 0.50 | 0.68 |
| Mg | 0.30 | 0.35 | - | 0.43 | 0.52 | - | 0.54 | 0.63 | - | 0.43 | 0.50 |
| Na | 2.60 | 2.74 | - | 3.85 | 3.48 | - | 3.05 | 3.38 | - | 3.17 | 3.20 |
| K | 0.20 | 0.22 | - | 0.69 | 0.42 | - | 0.16 | 0.18 | - | 0.35 | 0.27 |
| $SO_4$ | 1.75 | 1.97 | - | 4.20 | 2.34 | - | 3.20 | 3.96 | - | 3.05 | 2.76 |
| Cl | 3.45 | 3.97 | - | 4.60 | 5.14 | - | 3.70 | 4.25 | @ | 3.91 | 4.45 |
| DOC | 11.50 | 8.06 | - | 5.85 | 8.45 | - | 20.00 | 16.50 | - | 12.45 | 11.00 |
| N | 0.01 | 0.01 | - | 0.03 | 0.01 | - | 0.01 | 0.01 | - | 0.02 | 0.01 |
| Org. Anions: meq·L$^{-1}$ | 74.2 | 59.0 | - | 49.1 | 67.5 | - | 119.6 | 106.1 | - | 41.1 | 77.5 |
| Gran Alk: mg·L$^{-1}$ | -1.58 | -0.35 | - | 1.17 | 0.59 | - | -3.40 | -1.85 | - | -1.27 | -0.54 |
| Totals: | | | | | | | | | | | |
| Anions meq·L$^{-1}$ | 0.21 | 0.22 | - | 0.29 | 0.28 | - | 0.29 | 0.31 | - | 0.26 | 0.27 |
| Cations meq·L$^{-1}$ | 0.20 | 0.20 | - | 0.28 | 0.26 | - | 0.27 | 0.28 | - | 0.25 | 0.24 |

Differences between bog and fen means (Tables 5.3 and 5.4) significant at:
@ $p < 0.10$
# $p < 0.05$

* All units in mg·L$^{-1}$ unless otherwise indicated
** Significance levels of annual means not available

**Table 5.5. F-values for Differences in Peat Parameters Between Wetlands Compared To Differences Between Samples Within Each Wetland**

| | May | | September | | November | |
|---|---|---|---|---|---|---|
| | F-value | Prob | F-value | Prob | F-value | Prob |
| pH | 10.39 | 0.002 | 117.06 | 0.0001 | 16.87 | 0.0003 |
| H | 10.39 | 0.002 | 117.06 | 0.0001 | 16.87 | 0.0003 |
| Al | 33.31 | 0.02 | 33.07 | 0.0001 | 23.41 | 0.0001 |
| Fe | 6.11 | 0.01 | 8.48 | 0.004 | 0.83 | 0.59 |
| Ca | 47.06 | 0.0001 | 29.19 | 0.0001 | 4.15 | 0.03 |
| Mg | 1.78 | 0.21 | 36.86 | 0.0001 | 19.00 | 0.0002 |
| Na | 2.52 | 0.11 | 46.84 | 0.0001 | 1.87 | 0.20 |
| K | 63.64 | 0.0001 | 50.71 | 0.0001 | 69.82 | 0.0001 |
| $SO_4$ | 7.49 | 0.005 | 2.82 | 0.09 | 4.57 | 0.02 |
| Cl | 1.72 | 0.23 | 0.77 | 0.63 | 1.32 | 0.35 |
| Total C | 4.79 | 0.02 | 4.83 | 0.02 | 25.04 | 0.0001 |
| Total N | 1.80 | 0.21 | 11.3 | 0.001 | 1.42 | 0.31 |
| C/N | 11.37 | 0.001 | 8.04 | 0.004 | 8.44 | 0.0037 |
| CEC | 12.17 | 0.001 | 3.50 | 0.05 | 11.35 | 0.001 |
| Totals: | | | | | | |
| Anions | 6.91 | 0.007 | 1.93 | 0.19 | 1.88 | 0.20 |
| Cations | 3.76 | 0.04 | 47.61 | 0.0001 | 4.66 | 0.02 |

Prob = Probability of random occurrence

Overall, the data indicate that $SO_4$ cycling in Kejimkujik streams is not accompanied by significant $SO_4$ cycling in the soil chemistry of bogs and fens. However, $SO_4$ cycling in the streams still may be controlled by small changes in the $SO_4$ concentrations in the soil which are insignificant. Small changes in soil chemistry can produce very large changes in water chemistry, since the concentrations of elements in the soil are several orders of magnitude larger than the water. Further study of seasonal changes in $SO_4$ levels of the pore waters of wetlands in this area is required to establish if this is the case. An alternative explanation for the results may be that $SO_4$ levels in the streams are controlled more by inputs from surrounding upland areas rather than from the soils of wetlands.

Large increases in the organic anion concentration in the streams during the late summer in this area have been reported by Howell (1988). Production of organic acids appears to be related to the C/N ratio in the peat (Table 5.1). The C/N ratio declined significantly between May and November (Table 5.1), which corresponds with increases of organic anion concentrations in the streamwater (Table 5.2). The C/N ratio also indicates the oxidation rate of organic matter (Stevenson, 1982). As decay and oxidation occur, C/N decreases since C is consumed by microbial activity, while N is more conservative. Microbial decay produces byproducts such as organic acids, carbon dioxide ($CO_2$) and methane ($CH_4$). H and C/N are inversely related in a positive feedback process. As H increases, the level of microbial activity is depressed and C/N increases, accompanied by enhanced production of organic acids. C/N and its effect on H are influenced by the hydrologic cycle. During the late summer, the reported increases in organic anions likely occur because of drawdown of the water table and increased oxidation of carbon.

Concentrations of H were much greater in the peat compared to the streamwater. Organic acids are mainly concentrated in the boundary layer next to the solid material in the peat. Individual pH values for the peat showed a considerable range, varying between 2.6 (Heber Meadows Brook) and 3.9 (Mersey River). For the streamwater, pH ranged between 4.2 (Heber Meadows Brook) and 6.8 (Rogers Brook).

A larger number of significant seasonal changes in chemistry occurred in the streamwater than in the peat and at higher significance levels. All of the cations and anions, with the exception of Na and K, increased between May and November (Na and K both decreased during this period). Similar increases in the other ions have been reported by Howell (1988) for several of the streams and rivers in Kejimkujik National Park. By contrast, only H, Fe, Ca and N increased in the peat during this period.

If the water chemistry is calculated on a mass basis in $mg \cdot g^{-1}$ as is done for the peat, the seasonal changes in the water chemistry are very small in magnitude in comparison to the peat, and metal concentrations are several orders of magnitude lower in the water than the peat. This illustrates the very substantial storage effect of the peat. The largest differences occurred with Al and Fe, in which concentrations in the peat exceeded concentrations in the water by six and five orders of magnitude, respectively. Concentrations of Ca, Mg, K, Na and $SO_4$ were two to three orders of magnitude larger in the peat than in the water. Total cations and total anions were five and three orders of magnitude larger in the peat than in the water, respectively. Al comprised over 80% of the total cations in the peat, whereas in the streamwater it was only a small fraction of the total cations.

The very high ratio of cations to anions in the peat (67:1 in November and 95:1 in September) reflects the negative charge of organic colloids. By contrast, in the streamwater, a charge balance is maintained, conserving the electroneutrality of the medium. The relative abundance of metallic cations in the peat, determined from the annual means (not shown in Table 5.1), is Al > Fe > K > Na > Mg > Ca; with the values of 12.66 > 3.17 > 1.58 > 1.21 > 0.46 > 0.26 $mg \cdot g^{-1}$, respectively. By contrast in the streamwater, the relative abundance is Na > Ca > Al > Mg = Fe > K; with values of 3.19 > 0.63 > 0.57 > 0.47 = 0.47 > 0.29, $mg \cdot L^{-1}$, respectively. In the peat, the abundance follows approximately a lyotropic series reflecting the combined effects of the ionic radius and the charge density of the ion (Taliburdeen, 1981). The exception was the reversal of divalent Ca and Mg with monovalent Na and K. This suggests an overabundance of Na and K in the nutrient supply which is probably due to atmospheric deposition at these sites from the ocean.

## 5.5 CHEMICAL CHARACTERISTICS OF BOGS AND FENS

Several significant chemical differences were noted between wetlands classified as bogs (dominated by sphagnum vegetation) and wetlands classified as fens (dominanted by graminoid vegetation). The bogs included: Heber Meadows Brook, Atkins Meadow Brook and the lower site on West River (Figure 5.1). *Cladina stellaris, Cladina mitis, Cladina rangiferina, Sphagnum fuscum, Sphagnum rubellum, Sphagnum angustifolium* and *Polystrichum commune* characterize the lichen and moss layer. *Chamaedaphne calyculata, Kalmia angustifolium, Ledum groenlandicum, Kalmia polifolia, Empetrum nigrum* and *Oxycoccos macrocarpon* dominate the shrub and low shrub layer. The fens were characterized by various shrub and graminoid species with a noticeable absence of sphagnum vegetation, indicating more nutrient-rich conditions. *Carex stricta, Calamagrostis canadensis, Carex rostrata* and *Carex bullata* characterize the graminoid layer, while *Spirea latifolia, Myrica gale*, and *Alnus rugosa* are predominant in the shrub layer. *Osmunda regalis, Solidago* spp. and *Sphagnum angustifolium* are common.

Several significant distinctions (at $p < 0.10$) between bogs and fens were apparent in the peat chemistry; in particular for values of H, Al, Fe, Na, K, C/N ratio, ash content and total cations (Table 5.3). Large differences also occurred with Ca, C, and total anions but the significance levels were higher ($p = 0.10$ to 0.20). Values greater than $p = 0.10$ are not indicated in Table 5.3. Significant distinctions were much fewer at $p < 0.05$. There were almost no significant distinctions in the streamwater (Table 5.4) chemistry originating from bogs and fens. The streams and rivers drained a variety of bogs and fens, as well as upland vegetated areas. Their chemistry reflects this combined influence. Thus, no significant distinctions were expected - especially in larger drainage basins, although the different chemistry of bogs and fens could be reflected in the chemical inputs to small drainage basins.

Overall, bog peats showed annual H concentrations three times higher than fens, with bogs having a mean annual value of 0.912 $mg \cdot L^{-1}$ and fens a value of 0.275 $mg \cdot L^{-1}$. Concentrations of Al, Fe, Ca, Na and K in bogs were approximately half the value that they were in the fens, reflecting the more eutrophic nature of these wetlands. Mg, Cl, $SO_4$ and total anions did not show the annual or consistent seasonal distinctions between bogs and fens that were apparent with the other ions.

Although the CEC was significantly higher in the bogs than the fens, the total cation levels were lower, reflecting the more oligotrophic nature of bogs. Significantly higher C/N values for bogs suggests that carbon oxidation by microbial activity is also much lower in bogs. This is probably related to the higher H concentrations which are generally associated with sphagnum species, suppressing microbial activity. The successive invasion of wetlands by sphagnum vegetation acts in a positive feedback mechanism generating reduced alkalinity and encouraging development of oligotrophic conditions (Gorham *et al.*, 1987). Increased acidity and reduced oxygen levels associated with the invasion of sphagnum further diminishes the supply of base cations and enhances the competitiveness of these species over others (Goodwin and Zeikos, 1987). This also reduces the decomposition rate which, in turn, leads to further accumulation of peat and a gradual cutoff of the nutrient supply and establishment of oligotrophic, and eventually ombrotrophic, conditions.

Although studies have not conclusively determined all of the processes behind the succession from fen to bog, they have identified the characteristics of sites in transition. Surveys of peatlands in Sweden and Minnesota indicate a bimodal pH distribution of wetlands, with fens at pH 6 and bogs at pH 4. There are comparatively few sites at intermediate values. A similar bimodal distribution occurs in base saturation with most fen peats at values over 50% and bog peats at values less than 25%. Those wetlands at intermediate values are regarded as transitional to bogs (Gorham *et al.*, 1987) and may be considered as "poor fens". As wetlands change from minerotrophy to ombrotrophy, ash contents decline and base saturation drops to very low levels as the nutrient supply from ground and surface water is cut off. Fens with pH 5 or less, Ca concentrations in surface water less than 3.0 to 5.0 $mg \cdot L^{-1}$, and low base saturation (25% to 50%) are likely to be in transition to bogs (Gorham *et al.*, 1987; Gorham, 1953).

The chemical characteristics of the fens in this study indicate that they are well within the transitional category. The pH values and base cation levels are very low for these fens with graminoid vegetation (mean annual pH 4.58; Ca = 0.70 $mg \cdot L^{-1}$ from pore water measurements of the peat). In general, their pH and nutrient status suggests that they are more appropriately categorized as extremely poor fens (Sjörs, 1950). Wetlands in this category are regarded as most sensitive to anthropogenic input of acids (Gorham *et al.*, 1987). These fens do not have sufficient base cation reserves to buffer significant acid loadings. Gorham *et al.* (1987) suggest that acid deposition accelerates the positive feedback process described above, enhancing the successive invasion of sphagnum species. For example, *Sphagnum angustifolium*, an acidophyllic species, is present in many of the fens. *Sphagnum magellanicum* and *Sphagnum fuscum*, which are both strongly acidophyllic species, occur in isolated hummocks in some of the fens although the density of occurrence is still quite low. Overall, the low base status of the fens and the presence of *Sphagnum* spp. suggest that conditions are favourable for rapid vegetational succession of the more acidophyllic sphagnum species.

## 5.6 SUMMARY

Results of investigations in 1987 provide an overview of seasonal dynamics in wetland chemistry in Kejimkujik National Park. Significant seasonal changes occur within the peat with some of the major ions as well as pH. Seasonal changes in the acidity appear to be associated mainly with C/N and organic acid production rather than mineral acids associated with $SO_4$. A much larger and more significant number of seasonal changes occur in the major ion chemistry of the streamwater. In the water, seasonal changes in the acidity are associated with both $SO_4$, as well as organic anions.

Significant chemical distinctions in the major ionic constituents also occur between wetlands classified as bogs and those classified as fens. The fens, however, are generally very low in base cations and in pH, indicating that they are probably in transition to bogs. As such, they have little buffering capacity and are considered, therefore, to be sensitive to acid deposition.

# 6.0 EFFECT OF WETLAND SOIL WATER PROCESSES ON RECEIVING WATERS

## 6.1 SAMPLING AND METHODS

The third phase of the program addressed the question of whether relationships can be established between the seasonal changes in drainage water chemistry and the seasonal changes in wetland soil chemistry. It also dealt with the question of whether proximity to different wetland classes has a significant effect on drainage chemistry.

Sampling was carried out on two small headwater streams in Kejimkujik National Park: Atkins Meadow Brook and Heber Meadows Brook (1460 and 959 ha, respectively). Total wetland area (open and treed) occupies a large percentage of the total surface area of each basin (21.4% of Atkins Meadow Brook; 31.5% of Heber Meadows Brook). Water chemistry should, therefore, be directly influenced and dominated by wetland outputs, provided such relationships exist. Both of these streams are only a few metres wide at their mouth and drain into the west side of Kejimkujik Lake (Figure 6.1). The sub-basin drained by Atkins Meadow Brook is approximately 7 km long and contains 11.3% open wetland while Heber Meadows Brook is shorter (2 km) and contains slightly less open wetland (9.6%). Sampling on Atkins Meadow Brook was carried out on four wetland sites (numbered AB01 to AB04) located approximately equidistant between the mouth and the source of the stream (Figure 6.1). On Heber Meadows Brook, two wetland sites (HM01, HM02) were sampled, one at the mouth, and the other near the source of Heber Meadows Brook. Collection of the field data was carried out by helicopter due to the inaccessibility of several of the wetland sampling sites. The locations of the wetlands sampled, and individual site sampling stations on Atkins Meadow Brook and Heber Meadow Brook, and corresponding identification numbers are indicated on Figure 6.1.

The peat chemistry and vegetation characteristics of the wetlands sampled indicate that they can be divided into three groups: bog, fen, and transitional (poor fen), with sampling providing an equal representation of each group. This included two large and fully developed sphagnum bogs (AB04, HM01), one on each stream, as well as two graminoid fens (AB02, HM02), also one located on each stream. The two transitional wetlands are located on Atkins Meadow Brook. The one closest to the source (AB03) is a fen dominated by graminoid species which shows evidence of being in the early stages of transition to a bog, with isolated clusters of sphagnum vegetation. The second nearer the mouth (AB01) has progressed further in its development and appears to be more of a bog. It is dominated by sphagnum species with isolated patches of graminoids and is identified as a bog-fen transition.

Wetland classifications at the six sampling sites are summarized below:

| Location | Site (Figure 6.1) | Classification |
|---|---|---|
| Source | AB 04 | Sphagnum Bog |
| Intermediate | AB 03 | Shrub Fen - Transitional |
| Intermediate | AB 02 | Graminoid Fen |
| Mouth | AB 01 | Sphagnum Bog - Transitional |
| Source | HM 02 | Graminoid Fen |
| Mouth | HM 01 | Sphagnum Bog |

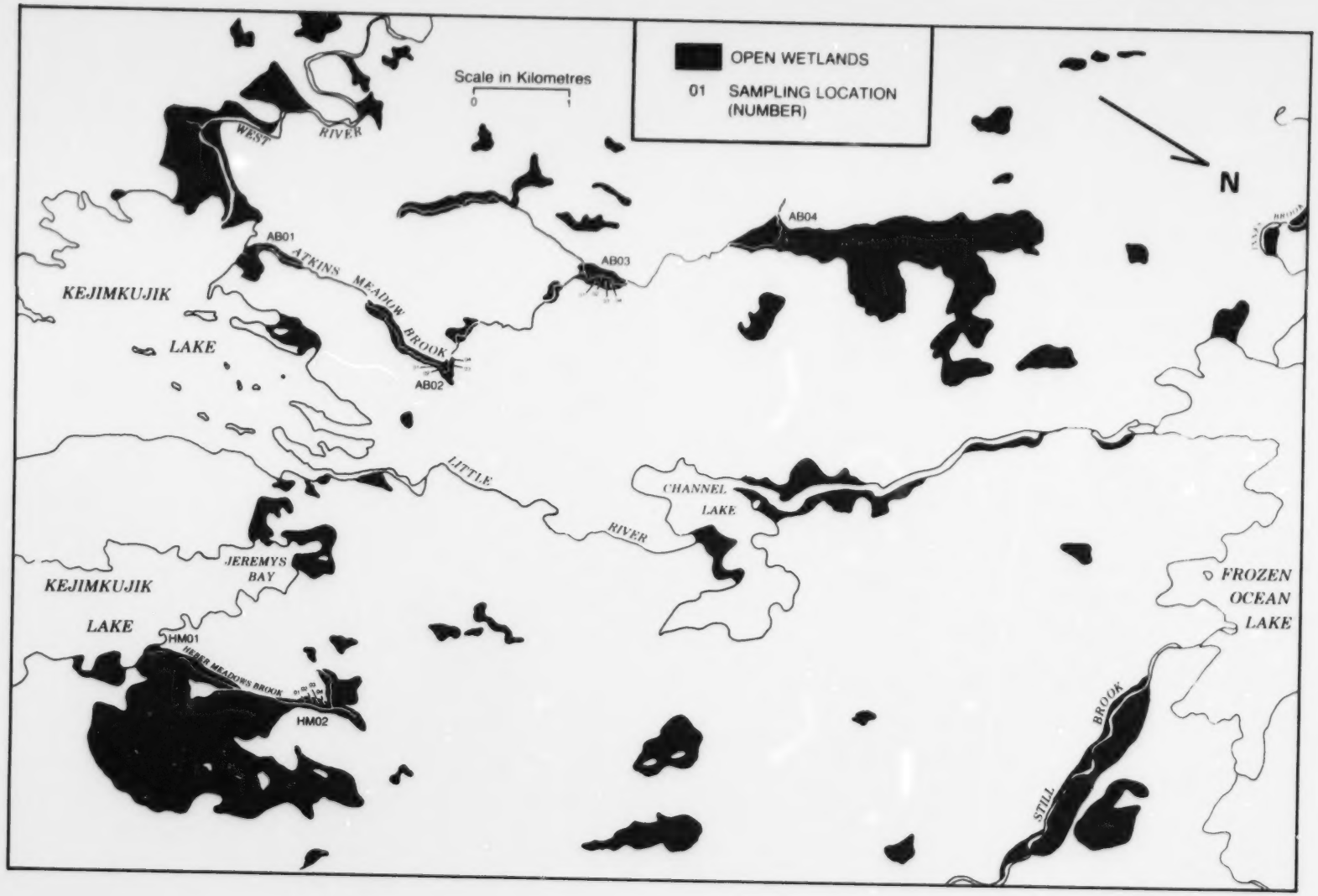


Figure 6.1. Peat sampling stations in Kejimkujik National Park, 1988.

The sampling locations were selected for two reasons: (1) to determine whether there is a progressive change in water chemistry downstream due to inputs from each of these wetlands; and (2) to determine whether there are localized changes in drainage water chemistry which reflect the differences in soil chemistry of the different classes of wetland. Since the wetland classes each have a markedly different chemical composition, local changes in water chemistry might be anticipated as the stream passes a fen or a bog, provided there are significant outputs of water from these wetlands.

Soil and water data was collected on April 26, June 2, August 2, October 12 and December 1, 1988. These dates were chosen to obtain a representative sampling of the stream chemistry during the maxima, minima, and intermediate positions on the rising and falling limbs of the seasonal cycles in DOC, sulphur and other major ions. Seasonal cycles in stream chemistry within the Park, including Atkins Meadow Brook, are described earlier in Chapter 5.1.

Soil sampling stations were located in the proximal zone within 10 metres of the stream banks. Each station was marked for repetitive sampling from the same precise location. Four sampling stations were selected for each wetland, spaced approximately 15 to 20 metres apart. A single 5-cm-diameter core was obtained at each station from the top 15 cm of the peat. In addition, four one-litre water samples were taken from the adjacent stream at locations corresponding approximately with the locations of the soil sampling stations.

Water samples were analyzed for the same constituents using the same procedures described in Chapter 5.2. Some of the procedures for analyzing soil samples were different to those described in Chapter 5.2, involving a number of improvements in the methodology and data yielded.

Sulphate and Cl were measured in the aqueous leach. The $SO_4$ and Cl concentration of the supernatant was measured by barium chloride ($BaCl_2$) turbimetric method and thiocyanate colorimetric method, respectively. Total sulphur was determined from the dried peat. Aqueous leach sulphur indicates how much sulphur is present in the pore water and is, therefore, available to form sulphuric acid in the peat, compared to the total sulphur reservoir (bound and exchangeable) within the solid peat material. Base saturation was also determined in addition to the cation exchange capacity (CEC). Base saturation (exchangeable Na + K + Ca + Mg / CEC) indicates the total reserve buffering capacity of the soil to acid inputs. Base saturation was determined from analysis of exchangeable Na, K, Ca, and Mg following a wash of dried soil in $BaCl_2 \cdot H_20$. The CEC was determined by a second extraction with HCl and barium acetate ($Ba(0Ac)_2$.

Carbon was measured by loss on ignition at 550°C. Peat soil samples were then freeze dried and processed through a ball mill and digested with nitric/perchloric acid. Ca, Mg, Al and Fe were determined by ICP mass spectroscopy, Na and K by atomic absorption spectrophotometry and total S by barium chloride turbimetric method. Total nitrogen was determined by the Kjeldahl method.

## 6.2 ANALYSIS

Chemical parameters for the peat (four cores per wetland) were averaged to obtain a single value for each wetland and then converted to the $\log_e$ side to reduce the variance (except pH, colour, alkalinity and base saturation). As a preliminary evaluation of the data, a series of plots was prepared of peat chemistry parameters versus the water chemistry parameters deemed most likely to be affected by changes in peat chemistry (Figures 6.2 to 6.11). If statistical relationships exist between the peat and corresponding drainage water chemistry, these would become evident from a visual analysis of these plots.

In these plots, peat parameters are plotted on the vertical scale and water parameters on the horizontal scale. The season in which the samples were collected is indicated by arrows connecting the points, the arrows indicating successively the direction of seasonal change (April 26, June 2, August 2,

October 12, December 1). The six wetlands sampled are identified by coded lines. The wetland identification number and classification are indicated on the legend. Site identification numbers correspond to the locations indicated on Figure 6.1.

The parameters plotted include: pH peat versus pH water (Figure 6.2); log C/N peat versus log DOC water (Figure 6.3); log C/N peat versus pH water (Figure 6..4); % moisture peat versus log DOC water (Figure 6.5); log total S peat versus log total S water (Figure 6.6); log total S peat versus pH water (Figure 6.7); log Ca peat versus log Ca water (Figure 6.8); log Mg peat versus log Mg water (Figure 6.9); log Fe peat versus log Fe water (Figure 6.10); and log Al peat versus log Al (Figure 6.11).

In addition to a visual analysis of the graphically presented data, analysis of variance (ANOVA) was carried out on selected peat and water parameters using SAS GLM to determine if there are significant differences in peat chemistry and drainage water chemistry with wetland class and with season. A nested ANOVA procedure with two crossed factors (Joyner, 1985) was carried out on parameters which are of special significance in controlling acidity. The peat variables tested were pH, C/N, % moisture content, total S and Ca. Water parameters tested include pH, DOC, S and Ca,. These variables were selected because of their potential to affect the acidity of the soil and water.

The C/N ratio indicates the degree of oxidation of carbon. This is generally controlled by the degree to which anaerobic conditions are established in the peat, which are, in turn, regulated by fluctuations in the water table. With drawdown of the water table, carbon is oxidized and declines in relation to nitrogen. Significant organic acid production might be expected as a byproduct, with corresponding higher levels of DOC in the drainage water. Similarly, S is oxidized by drawdown and, subsequently, may be flushed out of the peat as sulphuric acid ($H_2SO_4$) or as calcium sulphate ($CaSO_4$). Ca levels in the receiving waters may be regulated more by flushing from upland mineral soils, although some Ca may be flushed following drawdown and oxidation as $CaSO_4$ (Bayley *et al.*, 1986).

## 6.3 RESULTS

Figure 6.2 to 6.11 show a strong distinction in the chemistry of the different wetland classes (bogs versus fens). This is indicated by a wide separation between the bogs and fens on the vertical scale which represents peat chemistry parameters. The bogs (sites HM 01 and AB 04) and the transitional bog (site AB 01) tended to cluster toward distinctly lower pH values in the range 3.6 to 4.2 (Figure 6.2). The fens (sites AB 02 and HM 02) and the transitional fen (site AB 03) clustered at higher pH ranges 4.3 to 5.2. This also corresponds with much higher log C/N ratios for the bogs (3.7 to 4.4) than the fens (3.2 to 3.6), with the two transitional wetlands (Sites AB 03 and AB 01) falling at intermediate values(3.5 to 3.7). The bog peats clearly also tended to retain more moisture than the fen peats with the transitional wetlands again at intermediate values (Figure 6.5). This is likely because of the more porous nature of bog peats which undergo slower rates of microbial decay.

With regard to sulphur (Figure 6.6), the distinction was not as clear. The bogs generally had higher amounts of sulphur than fens, although one of the bogs (Site AB 04) had similar intermediate values to one of the fens (Site HM 02). The same pattern occurred with Ca and Mg (Figures 6.8 and 6.9), with the bogs clearly an order of magnitude lower than the fens except Site AB 04. This site had abnormally high levels of Ca for a bog, although it had normal low levels of Mg. The distinction was also not as well defined for Al (Figure 6.11), with one of the bogs (Site HM 01) at intermediate values close to the transitional wetlands, although the other bogs and fens were three orders of magnitude apart.

F-values from the ANOVA test are shown in Table 6.1 for selected peat and water parameters. The F-values on the left half of the table represent the ratio of the mean square of the differences between bogs and fens for a particular parameter, to the mean square of the error, or, on the right half, the mean square of the seasonal differences to the mean square of the error. High F-values indicate that

the differences due to season or wetland class are large relative to the random error. In general, the F-values confirm the observations presented in Figures 6.2 to 6.11. The F-values are very large and highly significant for the peat parameters pH, C/N, % moisture content, S, and Ca, and particularly for pH. This indicates very strong and significant differences in peat chemistry between bogs and fens, confirming the observations from the plots noted above and also the results presented in Section 5.5.

With the exception of pH, F-values (Table 6.1) indicate that seasonal differences in the peat were either not significant (e.g. % moisture content, Ca) or marginally significant (e.g. C/N, S). Overall, the F-values were much lower than the values for the differences between bogs and fens, suggesting that random variation is higher relative to seasonal differences. In general, F-values close to the minimum level for significant differences cannot be relied upon with any great confidence as a clear indication of differences between seasons.

**Table 6.1. F-Values for Differences Between Wetlands Classes and for Seasonal Differences for Several Peat and Water Parameters**

| | Peat F-value | | | Stream Water F-value | |
|---|---|---|---|---|---|
| Parameter | Bog-Fen | Seasonal | Parameter | Bog-Fen | Seasonal |
| pH | 1 037 | 15.4 | pH | 31.0 | 52 |
| C/N | 268 | 5.9 | DOC | 32.6 | 409 |
| % moisture | 116 | 1.4 | | - | - |
| Total S | 96 | 5.2 | S | 1.9 | 272 |
| Ca | 324 | 1.3 | Ca | 9.0 | 190 |
| F* | 7 | 3.5 | F* | 7.5 | 4.0 |
| F** | 4 | 2.5 | F** | 4.0 | 2.5 |

F* : F-value required for significant difference at p = 0.01.
F** : F-value required for significant difference at p = 0.05.

Significant distinctions are also evident graphically in Figures 6.2 to 6.11. Significant seasonal differences are indicated graphically by the degree of similarity in the relative magnitudes and relative direction of change (positive or negative on the vertical axis) for each wetland. For example, in Figure 6.2, although the magnitude of the change varies somewhat with each wetland, the variance in the relative changes in pH is visibly much less than the variance in the relative changes in % moisture content (Figure 6.5) or total S (Figure 6.6), where the changes are highly variable. This corresponds well with the higher F-values for pH and the low (non-significant) values for % moisture content and total S.

These observations and results, in a general way, confirm the findings presented in Chapter 5.4, in which significant seasonal changes in peat chemistry are reported for pH, as well as some major ions and total C, C/N, and CEC. In general, however, the seasonal aspect to the changes in peat chemistry is much less evident than it is for the stream water.

For stream water, F-values (Table 6.1) were large, indicating highly significant seasonal differences in pH, DOC, S and Ca. This is consistent with the highly significant seasonal changes in pH and major ions reported in Chapter 5.4 and also with the findings reported by Howell (1988).

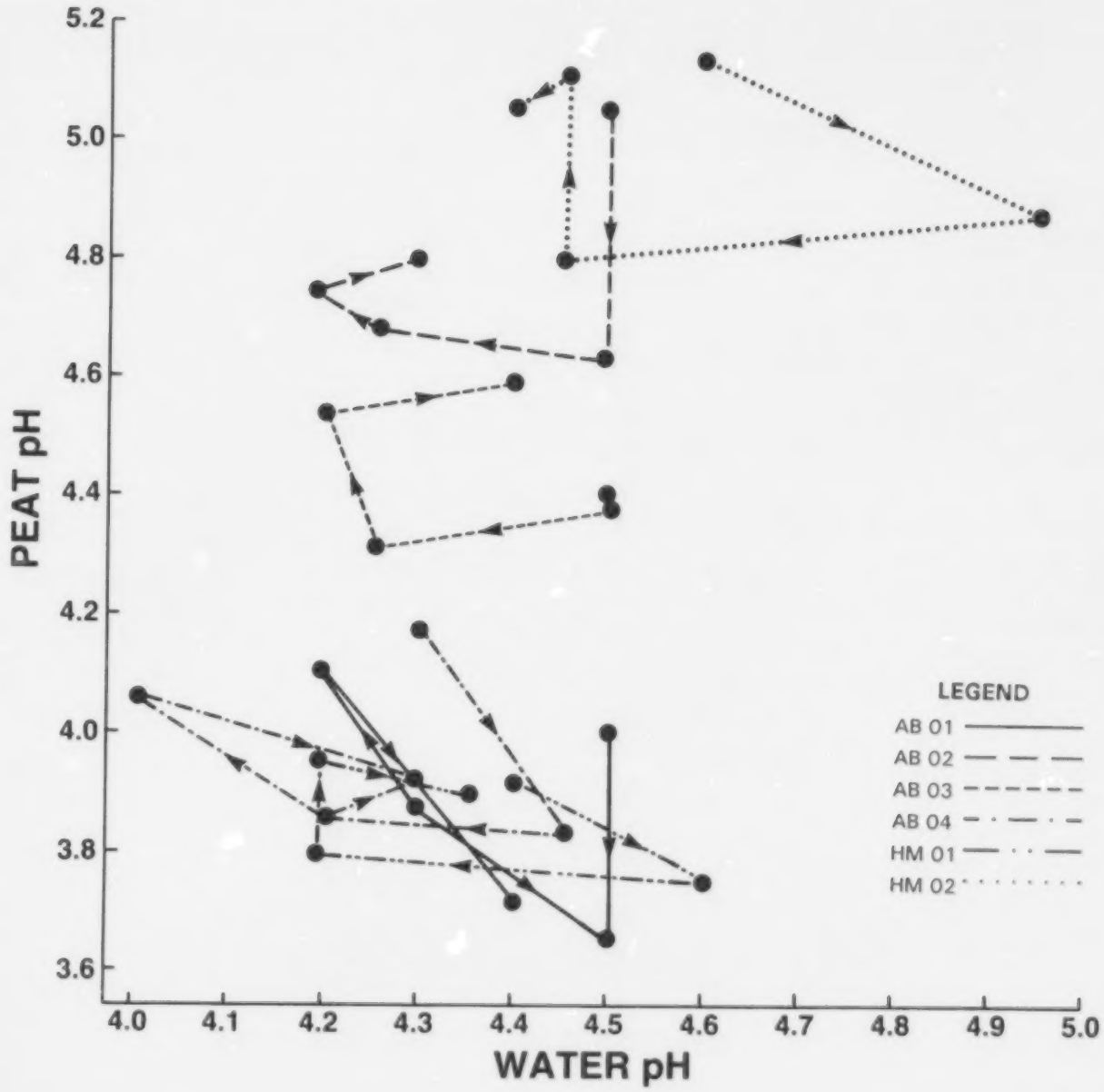


Figure 6.2. Relationship between stream-water pH and peat pH.

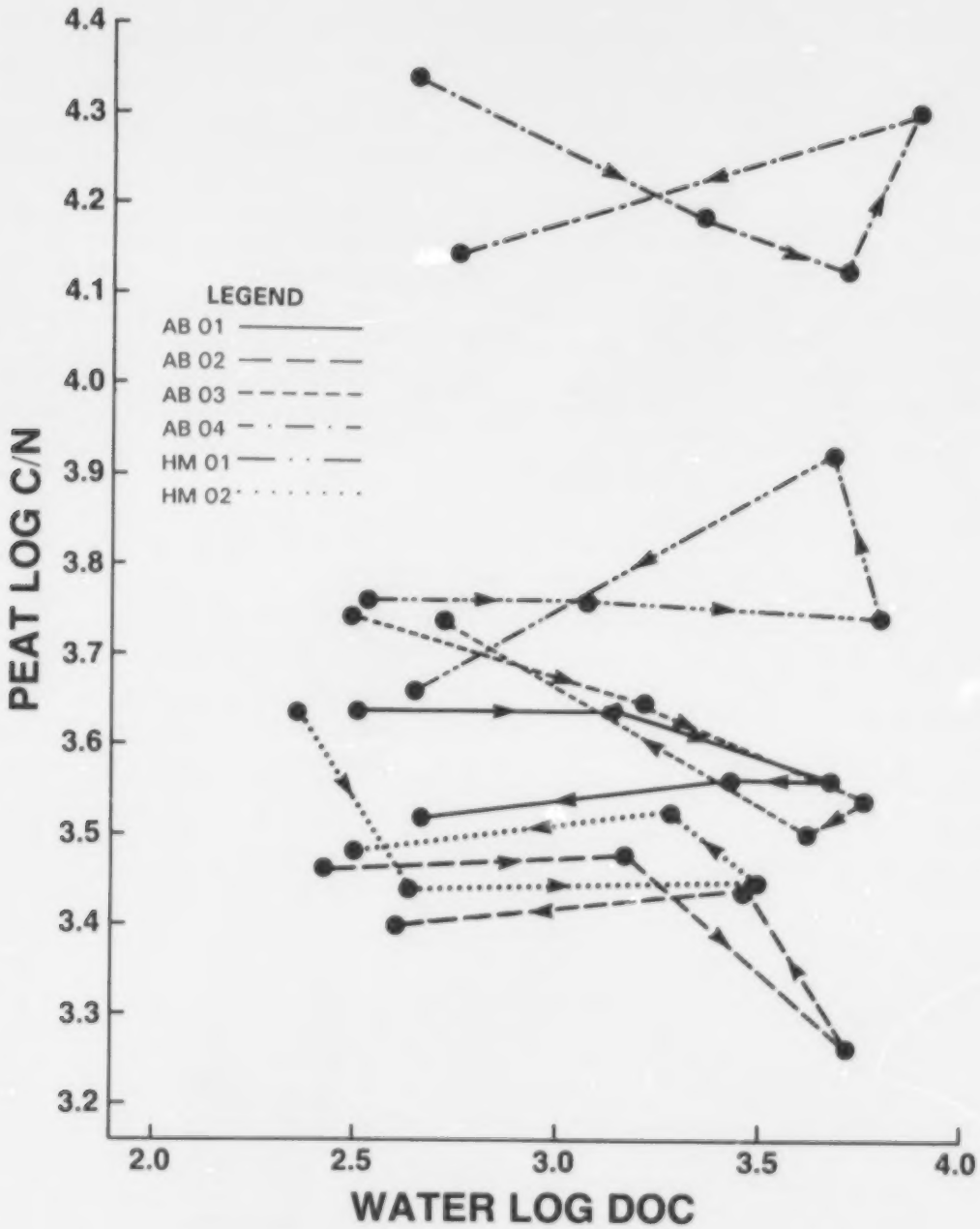


Figure 6.3. Relationship between stream-water DOC and peat C/N ratio.

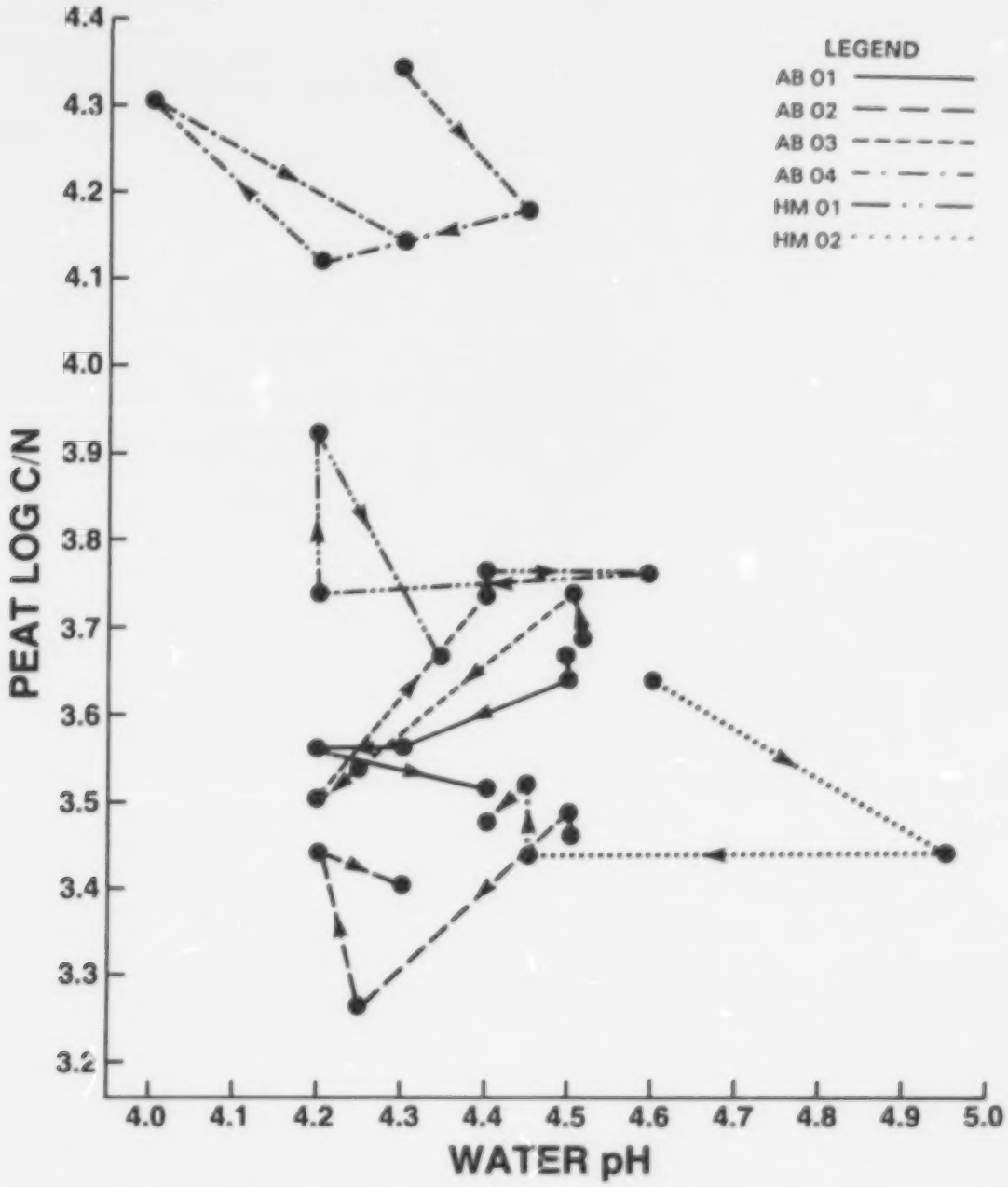


Figure 6.4. Relationship between stream-water pH and peat C/N ratio.

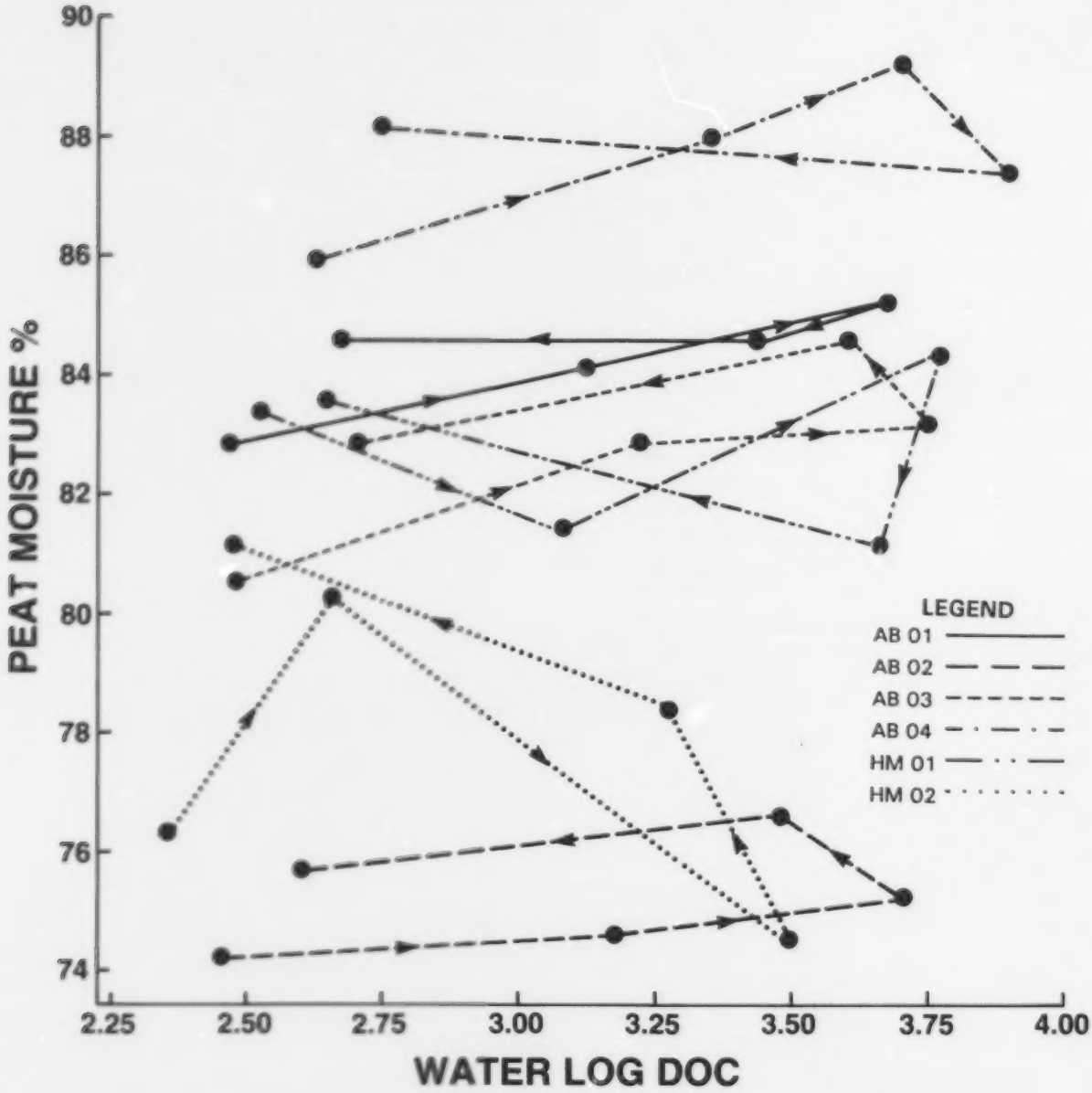


Figure 6.5. Relationship between stream-water DOC and peat moisture content.

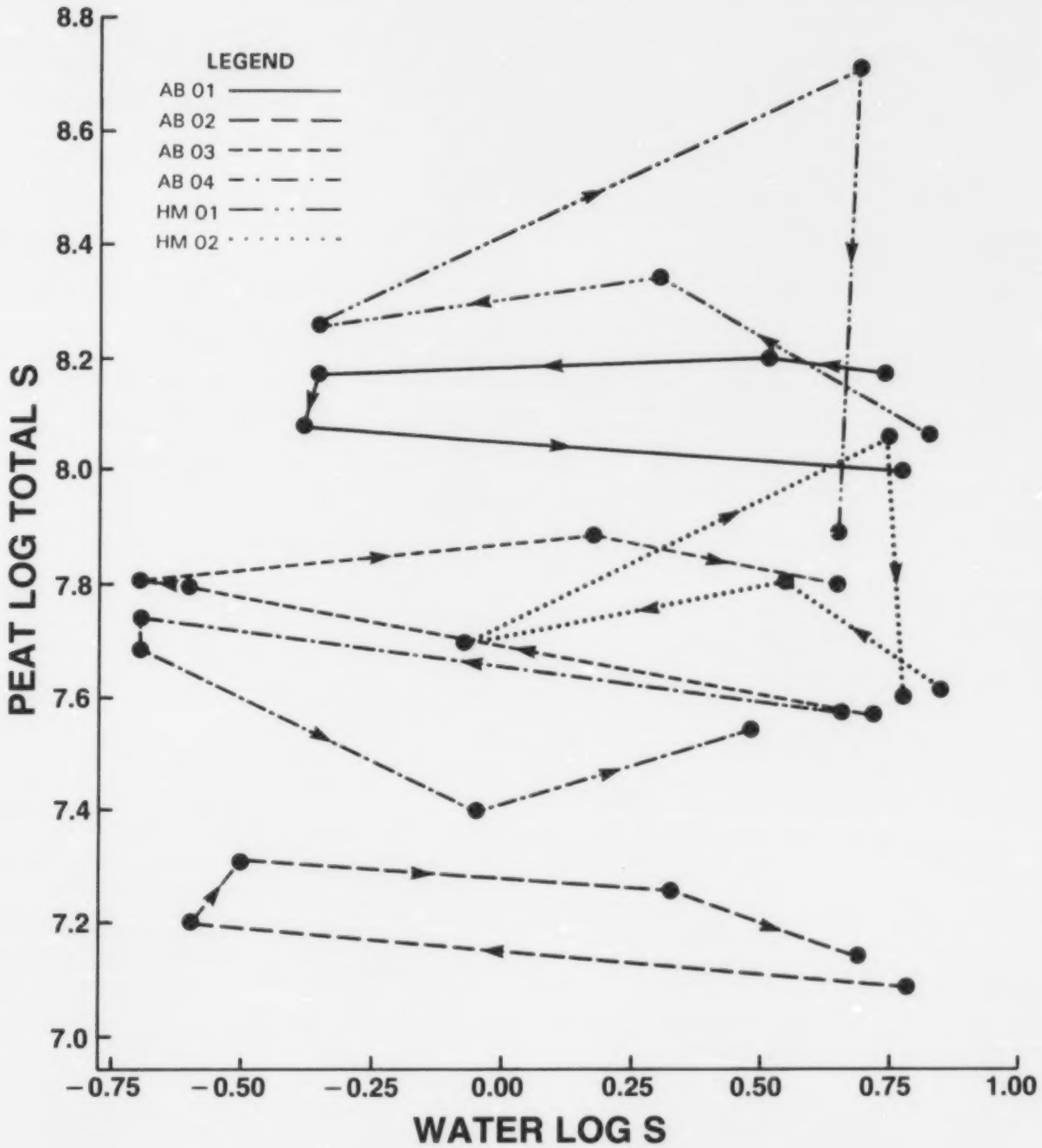


Figure 6.6. Relationship between stream-water S and peat total S.

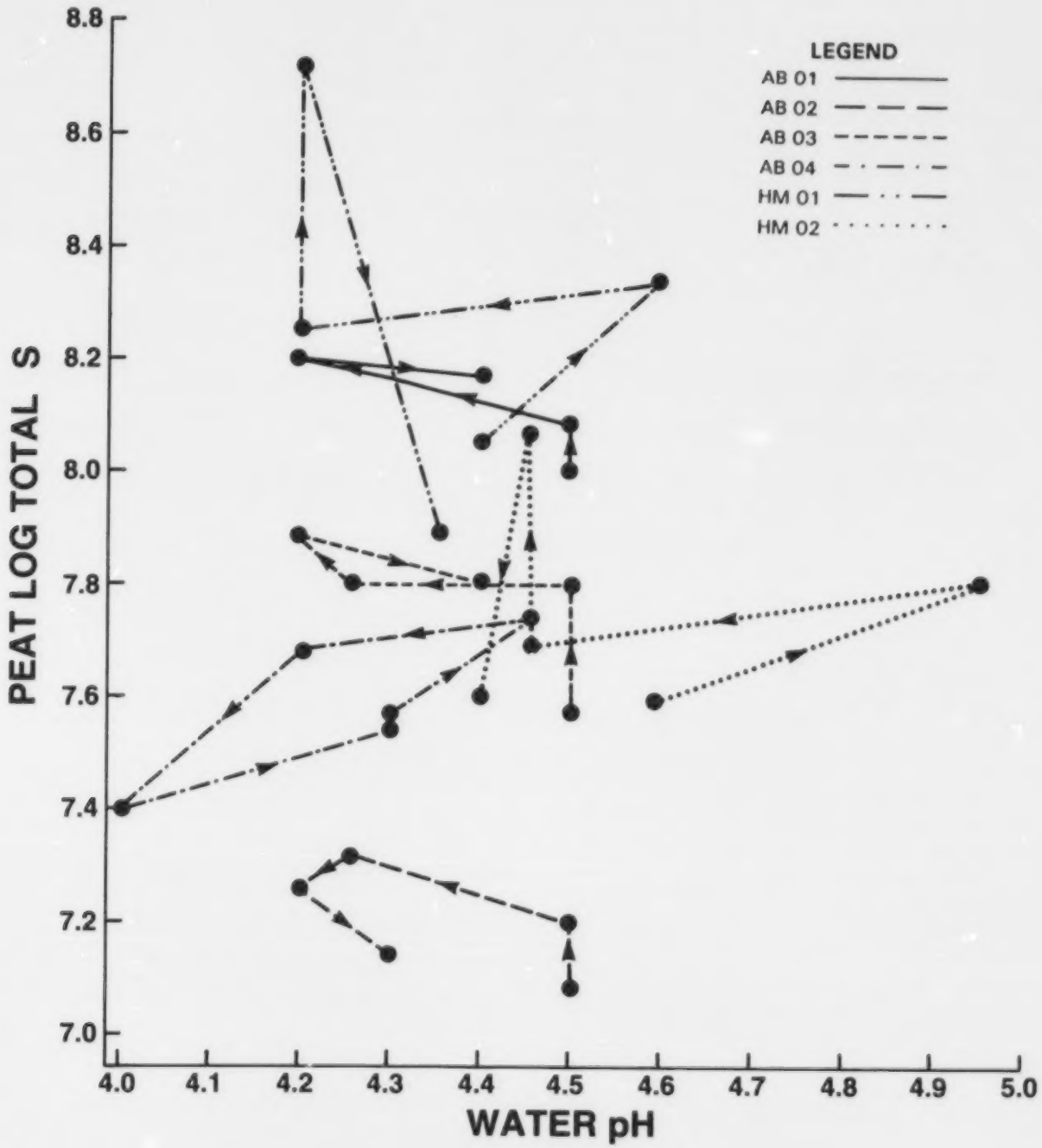


Figure 6.7. Relationship between stream-water pH and peat total S.

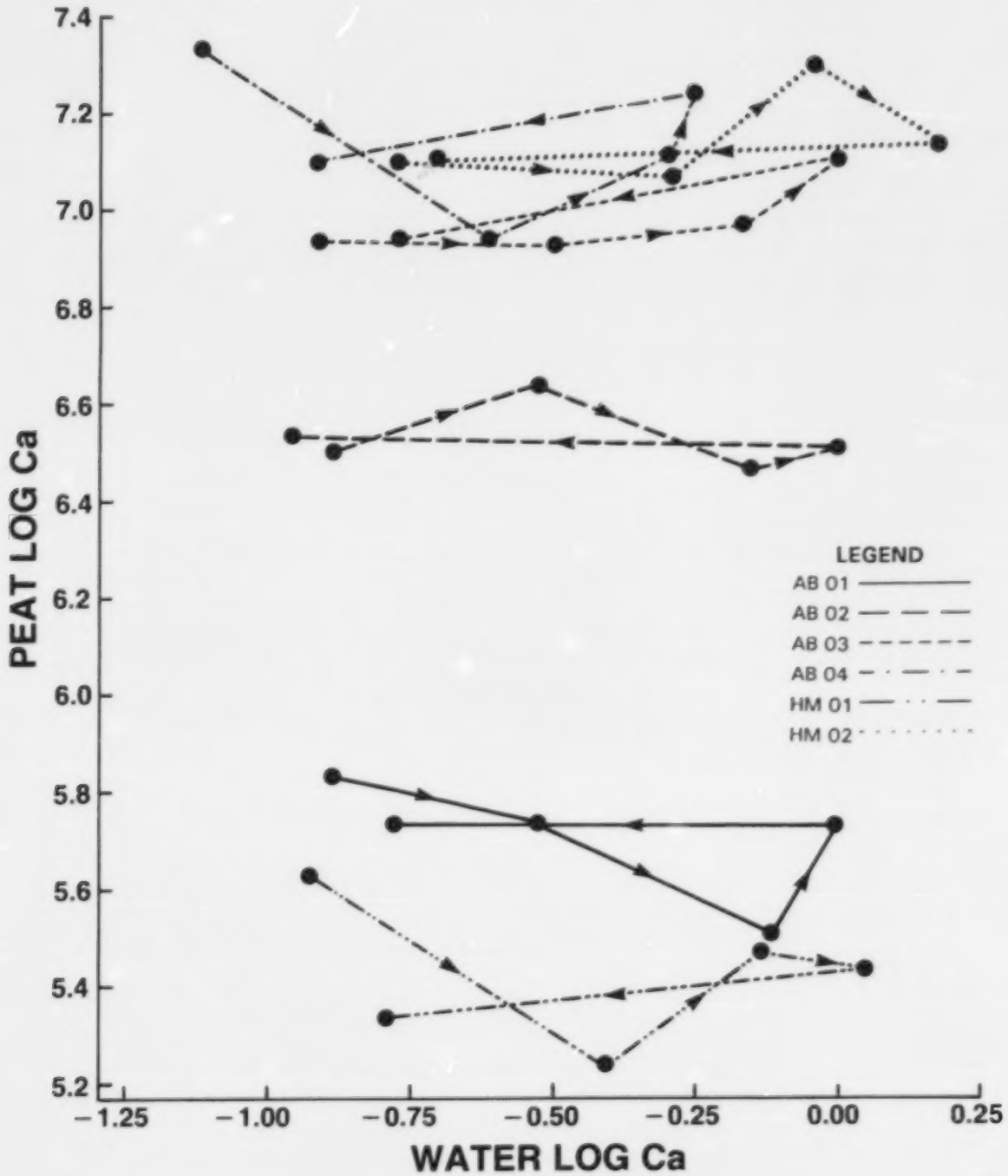


Figure 6.8. Relationship between stream-water Ca and peat Ca.

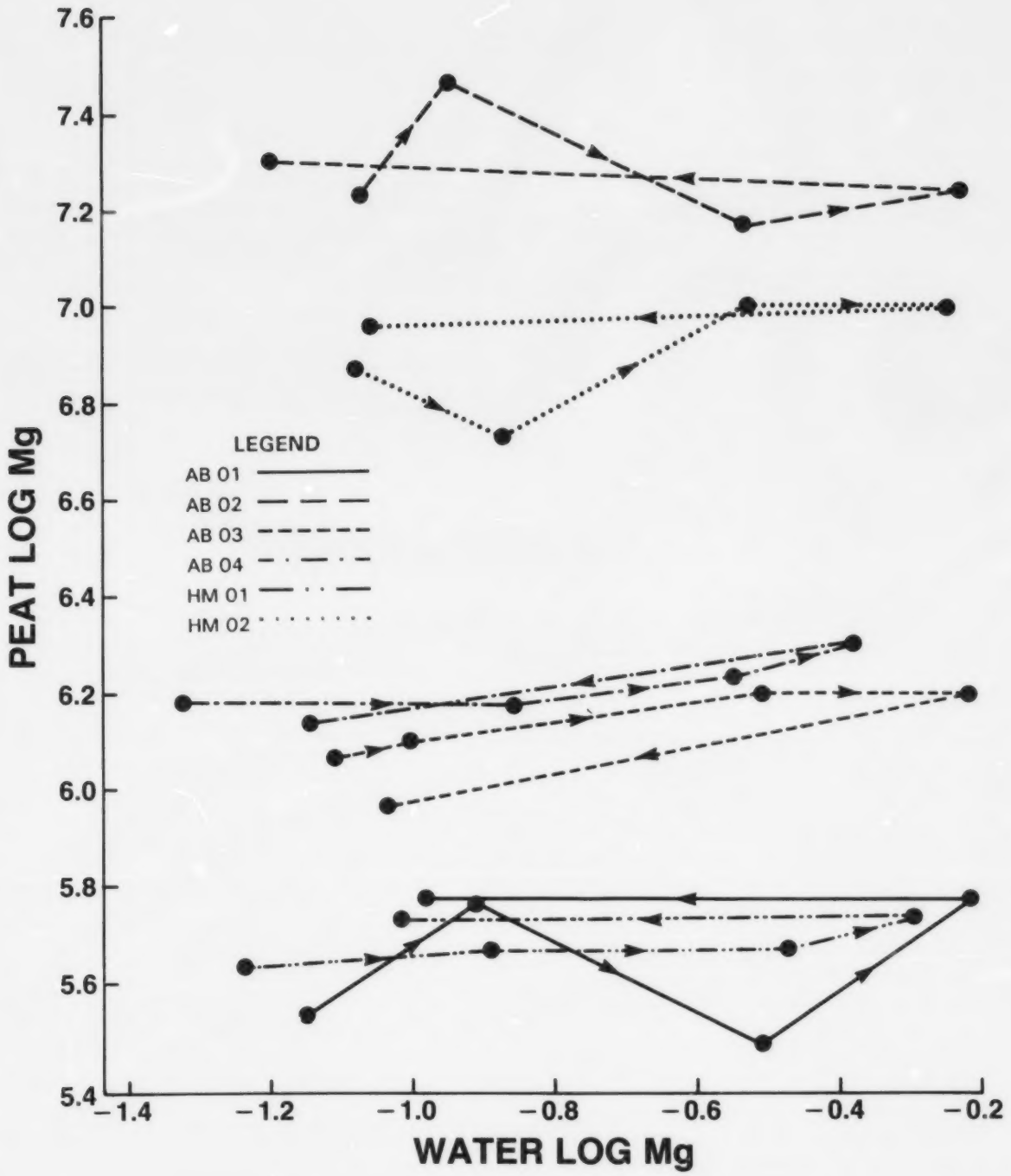


Figure 6.9. Relationship between stream-water Mg and peat Mg.

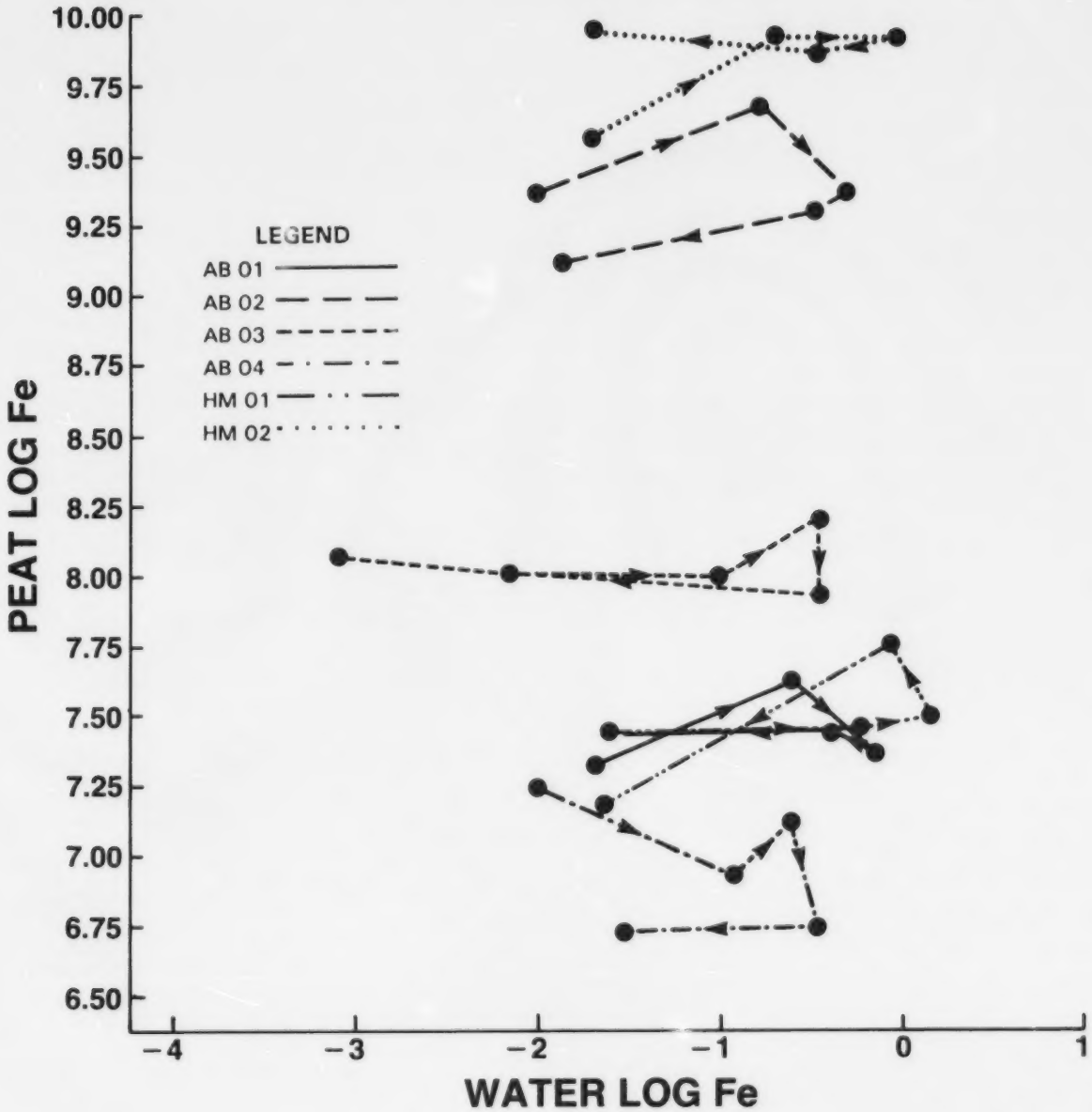


Figure 6.10. Relationship between stream-water Fe and peat Fe.

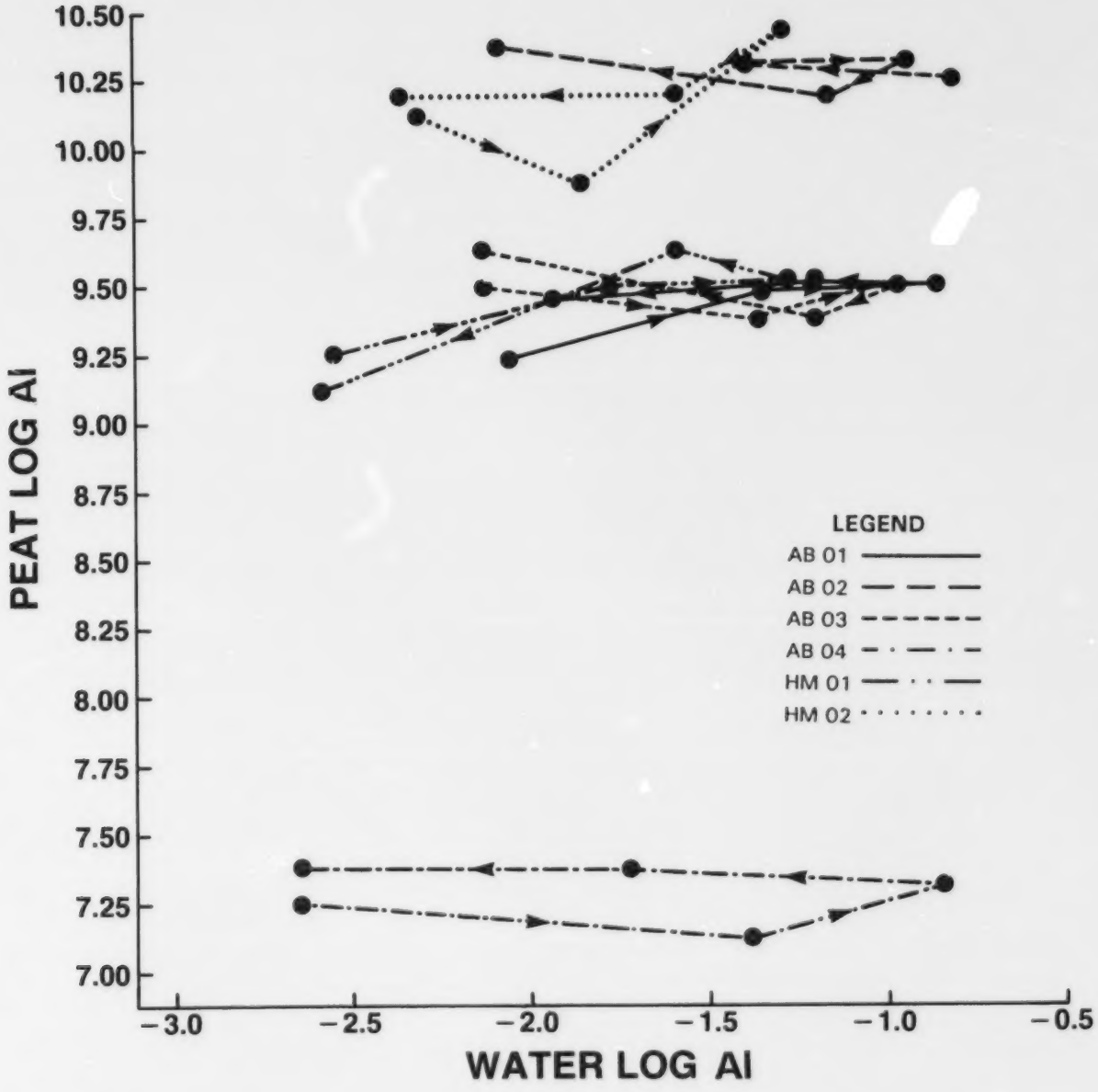


Figure 6.11. Relationship between stream-water Al and peat Al.

The high F-values for seasonal changes in water chemistry parameters are indicated graphically by a high degree of similarity in the relative magnitudes and general direction on the horizontal scale (position - right or negative - left) in Figures 6.2 to 6.11. This is apparent for DOC (Figure 6.3), total S (Figure 6.7) and Ca (Figure 6.8) and to a lesser extent for pH (Figure 6.2). Figures 6.10 and 6.11 suggest that significant F-values may also occur with Fe and Al.

A striking observation from the plots, for most of the parameters tested, is that there appears to be no significant relationship between the soil chemistry of the different wetland classes and the drainage water chemistry. The peat chemistry showed fairly distinct clustering on the vertical scale for most parameters, which, as discussed above, indicates significant differences in the chemistry of bogs and fens. However, in most of the Figures (6.2 to 6.11), the clusters were oriented vertically (vertical slope) with respect to each other, indicating no apparent relationship to the water parameters. An apparent slope in the clusters with respect to each other in a successive manner, from bogs to fens, suggests a potential relationship between wetland class and water chemistry for a particular parameter.

A slight slope is apparent between peat pH and water pH (Figure 6.2), peat C/N and water DOC concentrations (Figure 6.3) and between % moisture content of the peat and water DOC concentrations (Figure 6.5). The slopes are shallow, indicating relatively small increases in water pH and DOC concentrations with peat pH, C/N and % moisture content. Nevertheless, the slopes do indicate the possibility that some relationships may exist.

The observations from the plots are supported by the results of the ANOVA procedure shown in Table 6.1. F-values were much smaller for differences in water chemistry between bog and fen sites than for seasonal differences. The F-values, however, are clearly significant at the $p = 0.01$ level of significance for pH and DOC, and marginally significant for Ca. This implies that bogs and fens exert a significant local effect on the water chemistry of Atkins Meadow Brook and Heber Meadows Brook with respect to DOC inputs and its effect on pH, which is probably due to higher organic acid inputs from the bogs. Figure 6.3 suggests that DOC levels tend to be higher in bogs than fens, which is demonstrated by a slight slope in the clusters from fens toward bogs. In Figure 6.4, a negative slope is apparent, indicating that at the locations proximal to bogs, the pH of the stream water was lower than at locations next to fens. There was no obvious progressive trend from fens to bogs for S, Fe or Al (Figures 6.6, 6.10 and 6.11), nor was this clearly evident for Ca although the F-value ($F = 9$, Table 6.1) was marginally significant.

## 6.4 SUMMARY

With the exception of parameters related to organic acid production, there was little or no relationship between soil and water chemistry. It appears that major ion chemistry of streams is not much influenced by its proximity to these different wetland classes. There does appear to be a significant relationship between wetland soils and water chemistry associated with organic acid inputs. Bogs appear to contribute significantly higher organic acid inputs to these streams than fens - which is indicated by higher DOC levels and lower pH levels in the streams at these locations. The magnitude of the changes, however, is relatively small.

Water shows a very strong and significant seasonal aspect to its chemistry. In contrast, peat chemistry is not influenced much by seasonal changes, nor are the seasonal changes which do occur very large. This does not imply that there is no relationship between the seasonal chemistry of the two media because the concentration levels of the various parameters in the peat are several orders of magnitude larger than the levels in the water. Thus, a small seasonal change in peat chemistry could produce a large change in the water chemistry. However, there is no indication from the results that it is the wetlands which are responsible for the seasonal chemistry of the water. It seems likely that the water chemistry reflects an integrated seasonal effect from inputs over the entire basin.

# 7.0 CONCLUSIONS

The predominant wetland classes which occur in Kejimkujik National Park are bogs and nutrient-poor fens. Bogs and fens show distinct chemical differences, the bog peats being more oligotrophic, with the concentrations of metals and base cations being about half the level found in the fen peats. Carbon-nitrogen ratios of bogs are higher, indicating lower rates of carbon oxidation. The pH and major ions in the fen peats are generally low in comparison to the levels characteristic of true minerotrophic fens. This suggests that many of the fens are in transition to bogs and have a lower buffering capacity. This is confirmed by visual observations of the vegetation. Some of the fens investigated contained clusters of vegetation normally associated with bogs, in varying amounts, which indicates their transitional status. These wetlands are probably most susceptible to accelerated vegetational changes as a result of continued inputs of acid deposition.

The following conclusions can be made regarding the factors affecting the chemistry of wetland soils and their effect on drainage water chemistry within the Park.

(i) Despite the significant differences in soil chemistry between bogs and fens, proximity to these different wetland classes does not appear to influence major ion and metal chemistry of drainage waters.

(ii) Bogs and fens do show significant differences with regard to organic acid inputs to drainage waters. At locations proximal to bogs, dissolved organic carbon levels were significantly higher and pH was lower than at locations proximal to fens.

(iii) Drainage waters are dominated by a strong and significant seasonal aspect to their chemistry. With the exception of organic acid inputs, there is no evidence to indicate that this is related to processes occurring in wetland soils.

(iv) Although soil chemistry of the bogs and fens does show significant seasonal changes in some of the major ions, as well as pH and C/N, generally the seasonal changes are relatively small in magnitude and much less consistent than the changes in the drainage water.

(v) Overall, wetlands appear to have a significant but not necessarily a dominant effect on some aspects of the drainage water chemistry within the Park.

# 8.0 RECOMMENDATIONS

There are a number of factors which influence water chemistry which were not taken into consideration in this study. These factors include the effect of dilution/concentration processes, and also the effects of wetlands relative to other components of the drainage network. To assess the impact of these factors, studies of a more controlled or experimental nature are required. It is recommended that further studies involve:

(1) Detailed measurements of discharge throughout the drainage network.
(2) Detailed assessment of major ion outputs from wetlands and upland areas.

Discharge data for the various streams in the drainage network are necessary in order to separate changes in water chemistry owing to dilution/concentration effects (which are related to the hydrologic cycle) from direct inputs of dissolved organic carbon and other ions owing to processes occurring within the wetland ecosystem. Direct measurements of outputs of major ions from wetlands and upland areas would allow the relative role of wetlands to be assessed in relation to other significant components of the drainage basin, particularly the extensive areas of forested uplands. Evaluation of these two effects are a necessary first step toward developing numerical models of wetland effects on drainage water chemistry.

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